



Stability of vacancy clusters in nickel: A molecular statics study



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ABSTRACT

We report on the formation and stability of vacancy complexes in bulk Ni using molecular statics. Using an embedded atomic potential, we have investigated the effect of strain and temperature on their stability. At zero temperature our results compare favorably with first-principles calculations. The main effect of the presence of defects is a reduction of the elastic domain in comparison to the defect-free crystal, as well as an initiation of extended defects around the vacancy cluster at the yield point. All the clusters are found to be stable under the studied conditions, but the stability weakens with temperature, while strain may have opposing effects.

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1. Introduction

At equilibrium all materials are characterized by presence of vacancies. Although the equilibrium concentration of vacancies is in general small, extra concentrations may be generated by various processes when the material is acted upon by external agents, such as quenching, irradiation, oxidation, corrosion, and stress [1,2]. Condensation and configuration of vacancy clusters play an important role in the evolution of damage in a variety of materials. Their understanding is of great importance in estimating the lifetime of metals and alloys, and consequently, in looking for means to avoid their premature failure. Improving the durability of structures built from these materials involves understanding and controlling the diffusion mechanisms and interactions between vacancies and different species (oxygen, sulfur, carbon...) in solution inside the materials. Defects in a material, extended or localized, concentrate strain in their surroundings and therefore serve as precursors to crack nucleation. In particular, the possibility of deformation-induced dispersed vacancies to accumulate into vacancy clusters is clearly shown in nickel in Refs. [3,4]. Besides, aggregation of vacancies at grain boundaries are thought to play a role in the ductility dip characteristic of Ni and Ni-based alloys [5]. Moreover, the role of vacancies in the mechanisms of damage of nickel has been

considered in the literature, such as for example, ion irradiation damage [6], hydrogen embrittlement, stress corrosion and internal oxidation [7–10].

Thanks to their high resistance to oxidation and corrosion, nickel-based alloys have been extensively used in a number of technological applications, such as aeronautics and energy production [11,12]. In particular alloys 600 and 690 are used widely nowadays in nuclear energy production in pressurized water reactors, where they are subject to extreme conditions such as high temperatures and a highly corrosive environment. Many experimental and theoretical studies have been conducted on these kinds of alloys with the aim at optimizing their performance in time, and this by taking into account various parameters involved in the aging process, which are mechanical and physico-chemical in nature. As concerns the latter, influence of defects of the vacancy kind on the oxygen diffusion process in nickel, and consequently on the oxidation kinetics of the metal itself, has been shown experimentally [9,10]. The hypothesis put forth by these experimenters 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 [9,10]. These are the vacancies present initially in the alloy, but also the ones injected at the metal-oxide interface during the oxidation process.

As concerns interaction between oxygen and vacancies in nickel, Megchiche [13] and Mijoule et al. [14] have carried out *ab initio* simulations of Ni–O systems containing small vacancy clusters (monovacancy and divacancy). They have found evidence of strong interactions between the oxygen in solution in nickel

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with these kind of defects. These authors suggested that this interaction would play an important role in the oxygen kinetics inside nickel. This was shown to be the case later by *ab initio* calculations [15–17] as well as molecular dynamics simulations [18,19]. Preliminary results of our ongoing calculations concerned with oxygen segregation at vacancy clusters (mono-, di-, tri-, and tetravacancies) show substantial trapping capacities for oxygen atoms, and that this process depends strongly on the size and the geometry of the void formed by the vacancies. This accumulation of oxygen atoms inside a large void created in the nickel matrix has been observed recently in the MD simulations of Zou et al. [19].

Clearly, the prediction and control of all the phenomena mentioned above, requires an understanding of basic mechanisms of formation and clustering of vacancies and their associated kinetics. In general, however, many types of defects are present simultaneously in any given material. Consequently, this hinders experimental determination of the relevant parameters, such as formation and binding energies of the defects. In particular, the equilibrium concentrations of point defects in Ni are available only at the melting temperature [9]. In this sense, theoretical simulations of these kinds of defects are useful, either to compensate for the absence of experimental data, or equally importantly to come up with better alternative interpretations of established experimental results.

In this light, a study of the stability of these vacancy clusters, taking into account physical parameters that reproduce the real conditions of use of these materials, is therefore strongly called for. In the literature, and to our knowledge, there are only five theoretical works concerned with the processes of formation and stability of vacancy clusters in nickel [20–24]. In these works, the size of vacancy clusters was limited to six and the effects of mechanical strain have not been considered. All these theoretical works are obtained from calculations based on various semi-empirical methods, such as molecular dynamics calculations [21–23], calculations using embedded-atom potentials in the quasi-harmonic approximation [24], and empirical calculations [20]. In regards to *ab initio* calculations, we are aware of two works where thermal expansion effects were taken into account and were found to have an influence on the formation and binding energies of a single vacancy and a divacancy in Ni [25,26].

In the present paper we present an extensive study of small vacancy clusters (V_n , $n = 1$, until 19) in nickel. We consider their formation and binding energies in various configurations using embedded-atom potentials and classical molecular statics. We also investigate the effects of external parameters, namely, temperature and strain, on the stability of the vacancy clusters. The finite temperature calculations are conducted in the quasi-harmonic approximation. Where appropriate we will make comparisons between our results and those available in the literature.

The embedded atom model (EAM) potential used in this work has been shown to reproduce accurately the properties of Ni [27,28]. Use of *ab initio* methods to study vacancy clusters of the sizes studied in this work is beyond their capability within reasonable computational cost. Finite temperature free energy of defects can, in principle, be obtained using complex theoretical approaches, such thermodynamic integration [29] and metadynamics [30]. These methods are, however, computationally intensive, and as concerns nickel we are aware of only one work where the binding free energy of a divacancy is computed using thermodynamic integration [31]. On the other hand, approaches such as the quasi-harmonic method used in this work greatly simplify the work involved. This method is shown by Foiles [32] to yield results in agreement with the Monte Carlo method for temperatures up to half the melting temperature.

2. Methods

We have studied vacancy clusters in bulk fcc Ni employing a classical molecular statics approach, implemented in the LAMMPS [33] code, with an embedded-atom potential for the force field [27]. We have used periodic boundary conditions to generate an infinite crystal from a finite simulation box. The choice of the box size is made so that even our largest cluster has no interaction with its neighboring artificial images. To this effect we have checked the variation of the total energy of the system containing the largest cluster as a function of the box size.

It must be made clear, however, that for a given cluster size we consider only those configurations, among many, that have the lowest energy. Indeed for $n \geq 2$, there are many ways of realizing a cluster by choosing the relative positions of the monovacancies that form the cluster. For the simplest case of $n = 2$, the natural choice would be to put two monovacancies side-by-side, that is to remove two Ni atoms that are first nearest neighbors of one another from the perfect system. While this is true in general, and in Ni in particular, this configuration is found to be less stable in Al, for instance, as compared to the configuration where the monovacancies are located on the next-nearest neighbor positions [34]. We, therefore, must consider all the possible configurations of each given cluster of size n , to determine which one of them has the lowest energy for that particular size. In the case of Ni we have found that vacancies tend to create compact clusters, as opposed to what has been observed in Al, as mentioned earlier. Accordingly, we have made an inventory of all the likely stable configurations for each size n of the clusters. Total energies are compared at zero temperature to decide on the relative stability of the different inequivalent configurations of each cluster.

The most important quantities to look at in order to estimate the stability of various vacancy clusters are the formation and binding energies. At zero temperature the formation energy of a vacancy cluster of size n is given by

$$E_{nv}^F = E(N - n) - \frac{N - n}{N} E(N), \quad (1)$$

where $E(N)$ is the total energy of the perfect system with a simulation box containing N atoms, and $E(N - n)$ is the total energy of the system containing a n -vacancy cluster after relaxation of the atomic positions. In order to make comparisons between clusters of different sizes we use instead the formation energy per vacancy: $E_{nv}^f = E_{nv}^F / n$. The binding energy per vacancy for $n > 1$ is defined as $E_{nv}^b = E_{1v}^f - E_{nv}^f$. This quantifies the tendency of vacancies to bind together and form larger complexes. We represent in Fig. 1 the most stable configurations, we have found in this work, of a sample of n -vacancy clusters ($n = 2 \dots 15$).

At finite temperatures one must compare free energies instead of internal energies alone. The entropic terms become important and may indeed stabilize configurations that are otherwise unstable at 0 K. In fact there are two kinds of entropic contributions in our present system. First is the formation entropy of the vacancy clusters which is related to the change in the phonon spectrum upon introduction of the vacancy cluster to a previously perfect lattice. Second is the configuration entropy: this is geometric in origin and accounts for the many equivalent ways a cluster of size n can be realized with one site common to all. This quantity called g_{nv} is for instance equal to 6 for a divacancy and 8 for a trivacancy [35]. In order to obtain vacancy formation entropies, we have computed the phonon spectrum of Ni in the harmonic approximation, in absence as well as in presence of vacancies. We have obtained the phonon spectrum using the small displacement method [36] and direct diagonalization of the resulting dynamical matrix. The dynamical

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