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# Molecular dynamics simulations of the effects of vacancies on nickel self-diffusion, oxygen diffusion and oxidation initiation in nickel, using the ReaxFF reactive force field

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**Abstract**—A ReaxFF reactive force field was developed for the nickel–oxygen system. The quantum mechanical (QM) data used to derive the force field parameters included the equations of state of various phases of nickel and that of nickel oxide (NiO), the vacancy formation energy and the vacancy-mediated self-diffusion barrier in the face-centered cubic nickel. Furthermore, in order to study the interstitial diffusion of oxygen atoms in the nickel matrix, the oxygen insertion energies and the diffusion barriers were included in the training set. The force field was validated by performing molecular dynamics (MD) simulations of self-diffusion of nickel and the interstitial diffusion of oxygen. The predicted diffusivity and the activation energy achieved quantitative agreement with their respective published values. Furthermore, this force field enables study of the effects of vacancies on the diffusion of dissolved oxygen and the successive initiation of internal oxidation. A new oxygen diffusion mechanism is proposed in which the oxygen atom diffuses via the movement of the oxygen–vacancy pair. In addition, the MD simulation results suggest that the voids at the grain boundaries can induce local oxygen segregation due to the strong oxygen–vacancy binding effect, which is responsible for the formation of a nickel oxide particle in the void. These results demonstrate that the ReaxFF MD study can contribute to bridging the gap between the QM calculations and the experimental observations in the study of metal oxidation.

*Keywords:* Molecular dynamics; ReaxFF; Vacancy; Diffusion; Oxidation

## 1. Introduction

Nickel-based superalloys are applied in the energy industry [1–3] under extreme conditions such as high temperatures in conjunction with a corrosive environment. Compared with other metals, these materials exhibit good mechanical strength and resistance to corrosion at high temperatures [4]. Although such nickel-based superalloys have been studied extensively for many decades, there is still significant discussion regarding the fundamental oxidation mechanism of these materials [5].

The oxygen diffusion process is of great importance, because this process is at the origin of alloy oxidation and is partially responsible for the deterioration of the mechanical properties of metallic materials [6–8]. Several experimental techniques ([9], and the references therein) have been employed to measure the solubility and diffusivity of oxygen. Such techniques include internal oxidation, electron-stimulated desorption, electrochemical techniques and secondary ion mass spectrometry. However, the measured values for the diffusivity and the activation energy were found to be scattered over a wide range. Such uncertainties indicate large errors associated with these experimental studies.

Besides the experimental efforts in determining the diffusivity of oxygen in nickel, theoretical investigations have also been carried out on the subject using first-principles calculations. These calculations can determine the thermodynamic properties of materials and the kinetic parameters of chemical processes based on fundamental knowledge of the electronic structures. In the case of the interstitial diffusion of an oxygen atom in a dilute solid solution, the solution energy of an oxygen atom as well as the diffusion barrier can be obtained by performing first-principles calculations using relevant molecular models. In these calculations, the diffusivity is assumed to scale linearly with the jumping rate, which depends on the activation energy of each jump [10]. Previous calculations [11,12] have not considered the vacancy effect, and therefore underestimated the activation energy of diffusion. Recent studies [13,14] have demonstrated improved agreement with experimental observations by considering the effect of vacancies on oxygen diffusion. It has been shown that the strong binding effect between the oxygen atoms and vacancies will significantly increase the activation energy of the diffusion process and therefore decrease the mobility of interstitial oxygen atoms.

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However, the diffusion of oxygen during the oxidation process of nickel is much more complicated than interstitial diffusion. Perusin et al. [9] demonstrated that the grain-boundary (GB) diffusion of oxygen could play an important role in the oxidation of nickel. This short-circuit diffusion pathway could potentially lead to the formation of nickel oxide inside the voids of GB. First-principles calculations have difficulties describing these diffusion and oxidation phenomena at GB, because a large number of atoms are required to model the complex local environment of GB. The length scale of such a model is beyond the capability of quantum mechanical (QM) methods within reasonable computational cost. Furthermore, most of the QM calculations explore the potential energy surface of a particular system at 0 K. Thus, the dynamics of a system containing multiple atoms at high temperature such as the metal oxidation process are largely unaccounted for. First-principles molecular dynamics (MD) methods [15] have been employed to address this issue. However, the system scale and the time span of these simulations are highly restricted (∼100 atoms and several picoseconds, respectively), owing to the time-consuming electronic structure calculations.

To account for the gap (in both length and time scale) between experimental observations and theoretical calculations, simplified/empirical potentials have been developed and employed in MD simulations to predict material properties and to study their behavior at elevated temperatures. In these simplified potentials, the electronic degrees of freedom are frozen, and the interatomic interaction is described by empirical functions. Owing to their empirical nature, these functions contain parameters that need to be optimized against results obtained from higher levels of theory or experiments. The resulting potential can reproduce the potential energy surface within a certain accuracy, and hence be used to study static optimized geometry [16] and to explore system dynamics at high temperatures at a lower computational cost than the first-principles approach. In the case of metallic systems, the well-known embedded atom method (EAM) [17] is widely used in studying various properties and processes of both pure metals and multi-metallic alloy systems [18]. Hayat et al. [19] extensively studied the thermal properties of nickel metal using the EAM.

Despite its great success in providing a theoretical description of metallic systems, the EAM finds difficulties in simulating the oxidation phenomenon, because the potential function lacks the capability of describing the dynamic charge transfer between oxygen and metal atoms as well as the coulomb interactions between the resulting ions and cations. To address this issue, Zhou et al. [20] developed a charge-transfer ionic embedded atom potential that adds an extra energy term to the non-ionic energy terms of the EAM potential. The resulting potential features an electrostatic contribution and can be used to study the metal oxidation phenomenon. Variable charge molecular dynamics (VCMD) simulations of metal oxidation using this potential have been widely carried out on metallic systems such as nano-crystalline [21] and single-crystal [22] forms of aluminum, nickel–aluminum alloy [23] and the iron–aluminum–nickel ternary alloy system [24]. Specifically for the nickel–oxygen system, Garruchet et al. [25] studied the initial stage of oxidation on three different surfaces of nickel metal. The predicted oxygen surface coverage before the initiation of nucleation of surface oxide islands showed good agreement with experimental observations. In addition, the authors used this method to describe the interstitial diffusion of oxygen in the presence of lattice vacancies [26]. Furthermore, Elsener et al. [27] proposed a new charge optimization approach within the framework of VCMD that can significantly enhance the original potential in terms of computational savings. The authors have further applied the resulting variable-charge method in studying GB migration in the presence of interstitial oxygen atoms using a GB model containing ∼30,000 atoms [28].

In the current study, a ReaxFF [29] description of the Ni/O system was developed. The motivation of this work lies in the demonstrated higher accuracy of ReaxFF in describing diffusion phenomena in a single metallic system compared with that of the EAM potential [30]. In addition, ReaxFF features a charge calculation scheme (the Electronegativity Equalization Method [31], which is shielded for excessively high repulsion at close range [32]) that is similar to the charge transfer ionic model used in VCMD simulations [33]. This feature enables ReaxFF to describe the oxidation of metals. Furthermore, the formulation of the ReaxFF potential ensures the extension of the parameter set to more complex systems involving species other than $O_2$ molecules (e.g. $H_2$ and $H_2O$) that can be observed in a typical corrosive environment. For example, Russo and co-workers [34] reported a MD study on the use of the ReaxFF potential to model the interaction between aluminum clusters and water molecules. The transferability of the potential has been demonstrated by many successful applications of ReaxFF in describing covalent [35,36], metallic [37–40], ionic metal hydride [41–45] and metal oxide [46–48] materials. MD simulations employing the ReaxFF potential have been widely used to study the detailed chemical mechanisms related to scientific phenomena such as combustion [49–51], pyrolysis [52–57], catalysis [58–60], high-energy atomic collisions [61] and the processes undergone by nano-materials [62–64].

In the present work, the QM method used to generate data for force field fitting is briefly discussed. These QM data were reported in a recent publication [13] concerning the bulk diffusion of oxygen in nickel. The theoretically calculated oxygen diffusivity in the presence of a nearby vacancy based on QM data is supported by MD simulations using both the ReaxFF and the modified EAM potential. However, the diffusivity predicted using the ReaxFF potential was based on small systems (256 nickel atoms) and was associated with relatively large errors both in the diffusivity and in the activation energy. The present study systematically presents force field parameterization results related to the Ni/O system and the diffusivity studies involving larger systems, thus reducing the effects of size on the diffusivity. Multiple simulations are performed to measure the errors associated with the diffusivity predicted from MD simulations. Furthermore, a new oxygen diffusion mechanism is proposed based on the results of the MD simulations, as will be discussed in the following sections. Lastly, the force field is used to study the initial stage of vacancy-induced internal oxidation in nickel.

## 2. Computational methods

### 2.1. QM methods

QM methods for calculating the equations of state (EOS) of five types of crystal structure exhibited by nickel have been described in previous studies [38,59]. A similar