Oxidation of nickel surfaces through the energetic impacts of oxygen molecules: Reactive molecular dynamics simulations

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Molecular dynamics approach accompanied by reactive force field is used to study the characteristics of the oxide growth process on Ni(100) and Ni(111) surfaces at the temperatures of 300, 600, and 900 K and 5 eV as the energy of the O$_2$ impacts. The exposure of Ni surfaces to the high-energy O$_2$ impacts indicates that the primary oxide nuclei can be formed on any impact site. The results of kinetic studies clarify that the oxide growth kinetics cannot be accurately explained with the island growth model and increasing the surface temperature raises failure of the model. Under the present conditions, the growth kinetics is found to obey a Langmuir growth model. Increasing the surface temperature from 300 to 900 K results in $\sim$18.75% and $\sim$23% more oxygen consumption by (100) and (111) surfaces of Ni, respectively. The structure of nickel oxide (NiO) film formed after 200 successive O$_2$ impacts per surface super-cell is investigated utilizing radial distribution functions and oxygen density profiles. These calculations demonstrate that the structure of the formed NiO film is amorphous. Moreover, the charge profiles in Ni/NiO system are illustrated and discussed. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4945421]

I. INTRODUCTION

Nowadays, nickel is known as one of the most widely used materials playing a crucial role in manufacturing ferrous and nonferrous alloys. Nickel alloys possess high mechanical stability and can be used as heat- and corrosion-resistant materials in a vast variety of applied fields.$^{1-4}$ Also, nickel oxide (NiO) has technological importance in condensed matter physics, physical chemistry, and solid-state devices.$^{5-7}$

Due to the high demands for Ni and its alloys in various industries, its potential ability to reduce the costs caused by corrosion, and the technological use of NiO films, understanding the oxidation behavior of Ni has been the subject of many scientific researches. Various aspects of the interaction between Ni surfaces and oxygen species have been examined by means of different experimental and theoretical techniques.$^{8-19}$ The oxidation of Ni substrate via thermal oxygen species was addressed as the main concern of the scientific literature on the corresponding subject. However, hyperthermal oxidation has been less studied and requires comprehensive studies on the hyperthermal oxidation of Ni surfaces. In particular, the aerospace components are typically exposed to energetic particles at high temperature (e.g., O and O$_2$) and their performance is affected by subsequent hyperthermal oxidation. Therefore, study of the reaction kinetics during a hyperthermal condition is crucial to understand the reaction mechanism and to control the structure of the formed oxide.

It has been reported that the formation of NiO on Ni surfaces is carried out through three successive phases: fast chemisorption, rapid oxide growth, and slow oxide growth. This explanation was first verified for Ni(100) and Ni(111) surfaces by Holloway and Hudson.$^{20}$ They observed that Ni oxidation occurs through the nucleation and lateral development of oxide islands. According to their findings, NiO can be formed only at island perimeters. Sankaranarayanan and Ramanathan$^{11}$ and Garruchet et al.$^{10}$ studied the initial stages of Ni oxidation by variable charge molecular dynamics simulation. Their reports represented good agreement with the experimental results of Holloway and Hudson.$^{20}$

Zion et al. employed an in situ high-resolution electron-energy-loss spectroscopy in order to investigate the oxidation of Ni(111) surface by molecular oxygen in the energy range from 60 to 600 meV.$^{16}$ Based on their observations, the initial kinetic energy can affect oxide formation. They reported that most of the energetic impacted oxygen molecules link to the surface and the oxide nucleation may occur anywhere on Ni(111) surface. Major findings of this research were based on developing the Langmuir growth model to describe the oxidation kinetics of the Ni surface using high-energy O$_2$ beam.

Reactive force field (ReaxFF) based molecular dynamics simulations can be used to simulate chemical reactions in molecular and atomic systems. Reax is a bond order dependent potential model introduced in 2001 by van Duin et al.$^{21}$ Recently, this model has been extensively developed for many groups of compounds and successfully applied to study and simulate the oxidation of metals in the presence of different oxidizing agents such as O$_2$ and H$_2$O.$^{22-23}$

In the present work, we have carried out reactive molecular dynamics (RMD) simulations to investigate the hyperthermal oxidation kinetics of Ni(100) and Ni(111) surfaces at the temperatures of 300, 600, and 900 K. The
effects of surface temperature and crystallographic orientation on the oxidation kinetics were investigated through the study of the total oxygen uptake and the thickness of the NiO film. The oxide growth mechanism was determined by fitting the obtained kinetic data to the two kinetic models. The oxide structure was analyzed using the simulated trajectories. For this purpose, the radial distribution functions (RDFs), oxygen density profiles (ODPs), and charge profiles of NiO/NiO system were computed. To our knowledge, this work is the first molecular dynamics study on the hyperthermal oxidation of Ni surfaces at various temperatures. Fortunately, RMD can be used as a valuable tool to study a condition that is difficult to reproduce in other techniques. All simulations were performed using LAMMPS program package.

II. COMPUTATIONAL DETAILS

A. Potential model

The ReaxFF approach was applied to simulate hyperthermal oxidation process of Ni surfaces at various temperatures. ReaxFF captures the feature of the quantum chemical methods by employing many body potential terms. The corresponding equation of this potential model is expressed in Eq. (1). Energy terms including bond (\(E_{\text{bond}}\)), lone pair (\(E_{\text{lp}}\)), over/under coordination (\(E_{\text{over}}/E_{\text{under}}\)), valence (\(E_{\text{val}}\)), torsion angles (\(E_{\text{tors}}\)), van der Waals (\(E_{\text{vdw}}\)), and Coulomb (\(E_{\text{Coul}}\)) energies construct the total energy function (\(E_{\text{total}}\)),

\[
E_{\text{total}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdw}} + E_{\text{Coul}}.
\]

(1)

All the energy terms excluding the two non-bonded interactions (\(E_{\text{vdw}}\) and \(E_{\text{Coul}}\)) are computed based on the bond order between \(i\) and \(j\) particles (\(BO_{ij}\)). \(E_{\text{vdw}}\) and \(E_{\text{Coul}}\) are calculated between all atom pairs, regardless of bond-order and connectivity. \(BO_{ij}\) is calculated using Eq. (2).

\[
BO_{ij} = \exp \left[ p_{\text{bo}1} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{\text{bo}2}} \right] + \exp \left[ p_{\text{bo}3} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{\text{bo}4}} \right] + \exp \left[ p_{\text{bo}5} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{\text{bo}6}} \right],
\]

(2)

where \(r_{ij}\) stands for the interatomic distance and \(p_{\text{bo}1}\), \(p_{\text{bo}2}\), \(p_{\text{bo}3}\), \(p_{\text{bo}4}\), \(p_{\text{bo}5}\), \(p_{\text{bo}6}\), \(r_0\) are parameters representing the contribution of sigma, pi, and double pi bonds in the calculation of bond orders.

Variable atomic charges are implemented in ReaxFF adopting electronegativity equalization method (EEM).

The atomic charges are calculated at each iteration. A comprehensive explanation of the force field can be found in the literature. Force field parameters for description of Ni–O interactions were extracted from the work of Zou et al. The force field has been parameterized by a set of quantum mechanical (QM) data to appropriately treat nickel and nickel oxide in a range of chemical environments. The heats of formation of NiO and Ni_2O_3 were predicted by ReaxFF to be –37.8 and –70.15 kcal/mol, whereas those of DFT calculation were –24.2 and –82.15 kcal/mol, being in better agreement with the experimental heat of formation of –57.1 ± 0.3 kcal/mol corresponding to NiO.

B. Setup of the oxidation simulations

Ni(100) and Ni(111) surfaces were considered to perform the simulations. The size and shape of the surface super-cell were (9 × 9) and (7 × 7), respectively, and in the Z direction, eight atomic layers were used for nickel substrates. The standard crystalline form of the nickel is face-centered cubic (FCC) and the corresponding lattice parameter reported using ReaxFF has the value of 3.511 Å, which is in agreement with the experimental value of 3.524 Å. Different features of the simulated surfaces are given in Table I. First, the considered surfaces were connected to Berendsen thermostat during 20 ps in order to be equilibrated at 300, 600, and 900 K. The temperature control was performed using a damping parameter of 0.1 ps and the periodic boundary conditions were imposed only to the XY plane. The equilibrated surfaces were then relaxed in NVE ensemble for 10 ps. The second stage was initiated by exposing the surfaces to the hyperthermal oxygen molecules with high kinetic energy of 5 eV. The O_2 molecules were introduced in the box at regular intervals (2.5 ps) and placed at a distance of 15 Å above the surface. The impinging particle was directed normal to the surface, while the X and Y positions of each particle including the O_2 molecules were randomly selected. Before each new impact, the extra energy was removed using Berendsen thermostat. The equations of motion integration were performed adopting Verlet method with time step of 0.25 fs.

III. RESULTS AND DISCUSSION

A. Oxide growth on Ni(100) and Ni(111) surfaces in hyperthermal oxidation

1. Effect of surface temperature

The rates of oxygen consumption up to 200 impacts per surface super-cell on the Ni(100) and Ni(111) surfaces at three different temperatures of 300, 600, and 900 K are presented in Fig. 1. The consumption rate is defined as the total oxygen uptake versus the number of O_2 impacts per surface super-cell. For both studied surfaces, the oxygen uptake curve starts with a fast linear behavior and ends with a smooth nonlinear shape. The linear increasing rate is due to the high adsorption probability of O_2 molecules on Ni surfaces. The consumption rate increases until the NiO film reaches a certain thickness where preexisting oxygen atoms

<table>
<thead>
<tr>
<th>Orientations</th>
<th>Number of surface atoms</th>
<th>Number of Ni layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>(010)</td>
<td>(001)</td>
<td>(100)</td>
</tr>
<tr>
<td>(1-10)</td>
<td>(11-2)</td>
<td>(111)</td>
</tr>
</tbody>
</table>
reduce the attachment of further oxygen to the surface and the oxygen uptake begins to saturate gradually. In comparison with the literature, the observed oxygen uptake curves are qualitatively similar to what was seen in the work of Inoue and Teraoka.\textsuperscript{19} Their results indicated that the intermediate plateau in the uptake curve disappears for high energy incident of \(O_2\) beam.

The length of the linear part of each curve depends on the surface temperature. Clearly, increasing the surface temperature results in elongation of the linear part. Here, for the surface temperature of 900 K, the smooth nonlinear shape of the curves cannot be observed before 200 impacts per surface super-cell. The oxygen uptake curves for Ni(100) and Ni(111) surfaces at various temperatures were approximately similar up to 25 impacts per surface super-cell, characterizing the oxide onset exposure. This rapid stage in the uptake curves corresponds to the dissociative chemisorption in which \(O_2\) molecules dissociate and chemisorb on the surface. As can be seen in Fig. 1, this step is fairly independent of the surface temperature. Top view snapshots of the Ni/NiO system at the oxide onset exposure are given in Fig. 2. Subsequently, significant differences emerged in the uptake curves of the various simulated samples associated with the nucleation and oxide islands growth affected by the surface temperature. As the temperature of Ni(100) and Ni(111) surfaces increases, so do the oxidation rate also increase. The high surface temperature speeds up the oxidation rate and increases the mobility of oxygen species at Ni/NiO interface so that more oxygen ions can interpenetrate into the NiO film. Increasing the surface temperature from 300 to 900 K results in \(\sim 18.75\%\) and \(\sim 23\%\) more oxygen amounts on the NiO film for Ni(100) and Ni(111) surfaces, respectively. Moreover, the surface temperature was found to have more effects on the oxidation rate of Ni(111) surface. Top and side view snapshots of Ni/NiO system for 6 different simulated cases are depicted in Fig. 3. Since the oxidation rate of Ni surfaces increases with the increase of the surface temperature, a thicker NiO film is formed.

To evaluate the dependency of the oxide growth kinetics on the surface temperature, first, the oxygen uptake for Ni(100) surface at various temperatures was fitted to the island growth model, A second-order exponential function of exposure impacts per surface super-cell is given in Eq. (3)\textsuperscript{16,20}

\[
N(t) = N_{\text{sat}} - (N_{\text{sat}} - N_{\text{chem}})\exp\left[-K_1N_0(t - t_0)^2\right],
\]  

in which \(N(t)\) is the total oxygen uptake at \(t\) impacts per surface super-cell, \(N_{\text{sat}}\) is the saturation uptake, \(N_{\text{chem}}\) is the chemisorbed saturation uptake, \(K_1\) is the island growth rate constant, \(N_0\) is the density of nucleation sites, and \(t_0\) is the oxide onset exposure. This growth model is related to a mechanism where an oxide film develops via the nucleation and lateral growth of the oxide islands. As can be seen in Fig. 4, for exposure less than 100 impacts per surface

\[\text{FIG. 1. Total oxygen uptake during hyperthermal oxidation versus number of O}_2\text{ impacts per surface area at various temperatures (a) Ni(100) and (b) Ni(111).}\]

\[\text{FIG. 2. Top view snapshot of Ni/NiO system for Ni(100) at various temperatures taken at 25 impacts representing the oxide onset. Gray and blue spheres correspond to nickel and oxygen atoms, respectively.}\]
super-cell, at surface temperature of 300 K, the oxygen uptake data are well reproduced by this model. However, increasing the surface temperature decreases the capability of the island growth model to explain the oxidation kinetics. The calculated fitting parameters are given in Table II.

Then, the oxygen uptake was fitted to the Langmuir growth model which is expressed as follows:\textsuperscript{16}

\begin{equation}
N(t) = N_{sat} - (N_{sat} - N_{chem}) \exp[-K_2(t-t_0)],
\end{equation}

where \( K_2 \) is the Langmuir oxide growth rate constant. Compared to the island growth model, this model provides better fits at temperatures of 300, 600, and 900 K. The results of the fits to the Langmuir model are shown in Fig. 5 and the corresponding fitting parameters are summarized in Table III. Accordingly, one can conclude that the hyperthermal oxidation kinetics follows the Langmuir growth model corresponding to a mechanism where oxide forms anywhere on the surface not just at the island perimeters. These results are in good qualitative agreement with the results of Zion \textit{et al.} who observed that a Ni(111) surface at 300 K which is exposed to a relatively high-energy oxygen beam behaves according to the Langmuir growth model.\textsuperscript{16}

In summary, although the oxygen uptake at 300 K and low exposure is well fitted to the island growth model, significant deviation from this model is observed with increasing the surface temperature from 300 to 900 K, and consequently, the Langmuir growth mechanism is activated. In other words, the nucleation barrier and oxygen surface diffusion are of great importance in the oxidation of Ni surfaces and the oxide growth mechanism is affected by the one which is dominant. Here, due to the high-energy impacts, the required energy to pass the nucleation barrier is supplied and the oxide nucleation may happen on any impact site. Furthermore, increasing the surface temperature supplied the required energy for atomic motions at the interfaces facilitating atomic diffusion into NiO film. Hence, when the effect of high-energy impacts is

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Top and side view snapshots of Ni/NiO system after 200 impacts per surface area for 6 simulated samples. Gray and blue spheres correspond to nickel and oxygen atoms, respectively.}
\end{figure}
FIG. 4. Fits of the total oxygen uptake obtained from RMD using the island growth model for Ni(100) surface at various temperatures (a) 300 K, (b) 600 K, and (c) 900 K.

Coupled with high surface temperatures, the island growth model cannot describe the oxidation kinetics of Ni surfaces and the Langmuir growth model should be invoked. It should be mentioned that this finding is in fair agreement with the report of Zion et al.16

2. Effect of surface orientation

Fig. 6 shows the rate of oxygen consumption for different surface orientations. In the temperature range studied here, up to 200 impacts per surface super-cell, the rate curves for both surfaces are nearly similar and a slight difference is observed. From Fig. 6, Ni(100) surface exhibits slightly higher consumption rates over the Ni(111) surface in the low (300 K) and moderate (600 K) surface temperatures and at high surface temperature (900 K), both curves are the same. It was expected that the (100) surface is more reactive than the (111) surface because of the lower coordination of its surface atoms. Nevertheless, this difference in the reactivity was not clearly observed in the performed simulations, at least up to 200 impacts per surface super-cell. The partial dependency of the oxidation rate to the crystallographic orientation of Ni surfaces suggests that the oxide growth mechanism is independent of the surface crystallographic orientation. This effect was attributed to the high-energy of impacting particles that dominate the role of surface orientation.

Figure 7 displays the thickness of the NiO film versus the number of O\(_2\) impacts per surface super-cell. The Z coordinates of the most penetrated oxygen atom and the nickel atom with the highest Z value were subtracted to estimate the maximum thickness of the NiO film. For Ni(111) at 300 K, the thickness curve shows a fast increase in the thickness followed by a subsequent slow increase up to the saturation thickness limit. The saturation thickness for other studied cases is not reached up to 200 impacts per surface super-cell and to reach the saturation thickness more O\(_2\) impacts per surface super-cell need to be simulated. The thickness and the total oxygen uptake averaged over the last O\(_2\) impacts per surface

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ni(100) at 300 K</th>
<th>Ni(100) at 600 K</th>
<th>Ni(100) at 900 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{sat}}) (atoms)</td>
<td>182</td>
<td>214</td>
<td>250</td>
</tr>
<tr>
<td>(N_{\text{chem}}) (atoms)</td>
<td>41</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>(K_0/k_0)</td>
<td>(1.57 \times 10^{-4})</td>
<td>(1.55 \times 10^{-4})</td>
<td>(1.31 \times 10^{-4})</td>
</tr>
<tr>
<td>(t_0)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9642</td>
<td>0.9506</td>
<td>0.9187</td>
</tr>
</tbody>
</table>
super-cell are reported in Table IV. According to Table IV, the difference in NiO film thickness for Ni(100) and Ni(111) surfaces at 300 K, 600 K, and 900 K was 0.21 Å, 0.06 Å, and 0.02 Å, respectively. It looks that the observed difference is not significant and the trend can be changed by the way to calculate the thickness. The calculation method provides a rough approximation of the thickness. Therefore, due to the errors that may occur when calculating the oxide thickness, the total oxygen uptake was used to confirm the validity of the trend observed between Ni(100) and Ni(111) surfaces at different temperatures. To do this, the mean and the standard deviation of the oxygen uptake were calculated on 100 data point taken during the last O\textsubscript{2} impact for the 6 simulated samples. Also, the statistical t-test was performed on these data to verify the significant difference between the oxygen uptakes of the two surfaces. The results are given in Table IV that shows with increasing the surface temperature, the total oxygen uptake difference for Ni(100) and Ni(111) surfaces is decreased. Also, the calculated probability values of the t-test tend to zero indicating the oxygen uptakes of the two surfaces at different temperatures are significantly different from each other. Based on these calculations, it can be concluded that an increase in the surface temperature reduces the importance of the surface crystallographic orientation in the oxidation rate.

B. NiO film structure

1. RDFs

RDFs of the Ni–O pair in the NiO film are given in Fig. 8. For all considered samples, a sharp peak was seen around 1.8 Å in the Ni–O RDF representing the distance of the closest neighbor in the NiO structure, which can be compared with the measured distance of 1.9 Å for Ni–O bond length reported by

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ni(100) at 300 K</th>
<th>Ni(100) at 600 K</th>
<th>Ni(100) at 900 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{sat}$ (atoms)</td>
<td>296</td>
<td>368</td>
<td>1660</td>
</tr>
<tr>
<td>$N_{chem}$ (atoms)</td>
<td>32</td>
<td>36</td>
<td>46</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$5.52 \times 10^{-3}$</td>
<td>$5.03 \times 10^{-3}$</td>
<td>$8.55 \times 10^{-4}$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9890</td>
<td>0.9954</td>
<td>0.9968</td>
</tr>
</tbody>
</table>
FIG. 6. Number of reacted oxygen atoms during hyperthermal oxidation versus number of \( \text{O}_2 \) impacts per surface area for Ni(100) and Ni(111) at various temperatures (a) 300 K, (b) 600 K, and (c) 900 K.

FIG. 7. Thickness of the NiO film during hyperthermal oxidation versus number of \( \text{O}_2 \) impacts per surface area at various temperatures (a) Ni(100) and (b) Ni(111).

<table>
<thead>
<tr>
<th>Configuration of Ni</th>
<th>Average thickness (Å)</th>
<th>Standard deviation (thickness)</th>
<th>Average Oxygen uptake</th>
<th>Standard deviation (oxygen uptake)</th>
<th>Probability (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) at 300 K</td>
<td>7.02</td>
<td>0.25</td>
<td>194</td>
<td>2</td>
<td>0.000</td>
</tr>
<tr>
<td>(111) at 300 K</td>
<td>6.81</td>
<td>0.16</td>
<td>174</td>
<td>2</td>
<td>0.000</td>
</tr>
<tr>
<td>(100) at 600 K</td>
<td>8.55</td>
<td>0.20</td>
<td>226</td>
<td>2</td>
<td>0.000</td>
</tr>
<tr>
<td>(111) at 600 K</td>
<td>8.61</td>
<td>0.28</td>
<td>210</td>
<td>2</td>
<td>0.000</td>
</tr>
<tr>
<td>(100) at 900 K</td>
<td>10.63</td>
<td>0.43</td>
<td>271</td>
<td>1</td>
<td>0.000</td>
</tr>
<tr>
<td>(111) at 900 K</td>
<td>10.61</td>
<td>0.33</td>
<td>267</td>
<td>1</td>
<td>0.000</td>
</tr>
</tbody>
</table>

TABLE IV. Results of Ni oxidation after 200 \( \text{O}_2 \) impacts per surface area for 6 simulated samples.
Caputi et al. Moreover, another peak was detected around 4.5 Å corresponding to the distance of the second nearest neighbor in NiO structure (which was not shown in Fig. 8). Figure 8 showed that the surface crystallographic orientation does not have any considerable effect on the Ni–O RDFs. For various surface temperatures, RDFs were almost similar. However, increasing the surface temperature also increases the thermal disorders, which widen the first peak observed around 1.8 Å.

In order to determine the NiO film crystallinity, higher order peaks in Ni–O pair RDF can be analyzed. There are sharp peaks for higher order neighbors in RDF curve of the crystalline oxide. Figure 8 clearly showed that the oxide formed in all considered cases was amorphous.

2. Oxygen density profile

The ODPs for the two oxidized Ni(100) and Ni(111) surfaces are displayed in Fig. 9. Clearly, in the Ni/NiO system, peak intensities were observed to be slightly lower at higher surface temperature. Sharp peaks in ODP curves can be a measure of the NiO film crystallinity. In this way, one can conclude that the formed NiO film at lower temperatures is slightly more crystalline for both surfaces. An increase in the surface temperature reduced the intensities of the ODP peaks. Furthermore, as the surface temperature increased, the number of peaks and their width also increased showing the deeper penetration of the reacted oxygen atoms as well as greater atomic movement. Also, the ODP curve showed that the thickness of the NiO film formed on the Ni substrate at higher surface temperatures is greater than those corresponding to the lower temperature cases. Although, at higher temperatures, the oxide film has a more uniform distribution, it has an amorphous structure.

3. Charge profiles in Ni/NiO system

After 200 O₂ impacts per surface super-cell, the charge profiles of Ni and O species along the oxidation direction were analyzed for Ni(100) surface at temperatures of 300, 600, and 900 K as shown in Fig. 10. The charge profile is determined as the partial charge of each atom versus its Z-coordinate in Ni/NiO system. The partial charge of Ni atoms in the bulk Ni substrate oscillated around zero value and the positive and negative charges is assigned to reacted nickel and oxygen atoms, respectively. The approximate maximum charges of Ni and O atoms in the formed NiO film were 1.3e and −1.4e, respectively. Charge profiles were almost the same for Ni(100) and Ni(111) at the studied temperature ranges.

For all cases considered, the oxygen atoms at the NiO/Ni and O₂/NiO interface had smaller charges compared with those at the middle of the NiO film. The smaller charges...
FIG. 10. Charge profile in Ni/NiO system for Ni(100) at various temperatures (a) 300 K, (b) 600 K, and (c) 900 K. Electron charge is $e = 1.6 \times 10^{-19}$ C.

indicate the ionization of oxygen atoms by weakly charged cations at the NiO/Ni interface and ionization by insufficient concentrations of cations at O$_2$/NiO interface. Therefore, depending on the coordination number and the surrounding environment of each atom, the atomic charges were not homogeneous in the NiO film. Nevertheless, enhancing the surface temperature improved the charge homogeneity.

The partial charges of the reacted O atoms seem to involve two charge groups separated by an approximate gap of 0.3$e$. The more negative charges represent the reacted O atoms belonging to the NiO film. The less negative charges in Fig. 10 correspond to the partially ionized oxygen molecules trapped in the NiO film. The number of O atoms belonging to this group is found to reduce when the surface temperature is increased. It means that the number of the reacted O atoms having maximum charge increased with the increase of the surface temperature.

IV. CONCLUSIONS

Exposure of Ni surfaces to the energetic O$_2$ impacts was simulated at 300, 600, and 900 K using ReaxFF. Investigation of the oxidation rate curves revealed that the surface crystallographic orientation has a little effect on the oxidation rate. This can be mainly attributed to the high-energy impacts, which disrupt the effect of the surface crystallographic orientation. On bombarding Ni surfaces with energetic O$_2$ impacts, the high energy of the impacting particle overcomes the nucleation barrier, leading to the nucleation onset on any impact site. Moreover, increasing the surface temperature was accompanied by an increase in the oxidation rate of Ni surface. Thus, both factors, i.e., the oxygen uptake and the NiO film thickness increased at high surface temperatures. In order to investigate the surface temperature effect on the oxide growth mechanism, the simulated kinetics data were fitted to island and Langmuir growth models. Under the present conditions, the island growth model fails to describe the oxidation of Ni surfaces correctly. The most deviation from the island-growth model was observed at the temperature of 900 K. The oxidation kinetics is found to follow Langmuir growth model. Several criteria including RDFs, ODPs, and the charge profiles of Ni/NiO system were evaluated to characterize the structure of the formed NiO film. In all considered cases, the results of the calculated Ni–O RDFs and ODPs confirmed the amorphous structure of the formed NiO film. Analyzing the ODP curves also indicated that increasing the surface temperature reduces the NiO film crystallinity while improving its uniformity.

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