Deciphering atomistic mechanisms of the gas-solid interfacial reaction during alloy oxidation

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Gas-solid interfacial reaction is critical to many technological applications from heterogeneous catalysis to stress corrosion cracking. A prominent question that remains unclear is how gas and solid interact beyond chemisorption to form a stable interphase for bridging subsequent gas-solid reactions. Here, we report real-time atomic-scale observations of Ni-Al alloy oxidation reaction from initial surface adsorption to interfacial reaction into the bulk. We found distinct atomistic mechanisms for oxide growth in O\textsubscript{2} and H\textsubscript{2}O vapor, featuring a “step-edge” mechanism with severe interfacial strain in O\textsubscript{2}, and a “subsurface” one in H\textsubscript{2}O. Ab initio density functional theory simulations rationalize the H\textsubscript{2}O dissociation to favor the formation of a disordered oxide, which promotes ion diffusion to the oxide-metal interface and leads to an eased interfacial strain, therefore enhancing inward oxidation. Our findings depict a complete pathway for the Ni-Al surface oxidation reaction and delineate the delicate coupling of chemical-mechanical effect on gas-solid interactions.

INTRODUCTION
Gas-solid reactions are central to many technological processes, including stress corrosion cracking (1–4), hydrogen embrittlement (5, 6), and heterogeneous catalysis (7–11). These reactions generally initiate via gas adsorption, followed by nucleation and growth of a new phase, whereas canonical models are traditionally based on gravimetric measurements that oftentimes exclusively consider the growth process only. Moreover, new phase formation generates a new heterointerface between the base solid and newly formed phase that can play an important role in the subsequent reaction processes. For instance, epitaxial oxide formation on an alloy surface produces an interfacial strain that can result in cracking and/or spalling of the oxide layer, and cracks or strained intergranular paths will affect the ion diffusivity and lead consequently to an altered, often accelerated, oxidation rate. These coupled mechanical-chemical effects can markedly affect the oxidation- or corrosion-resistant properties of alloys and also lead to a sudden mechanical failure of alloys (12, 13). These mechanically coupled chemical processes are also found in other gas-metal interactions, i.e., the compressive strain in supported metal nanoparticle catalysts can largely enhance the catalytic activity of the metal (e.g., Pt) due to a shift of the electronic band structure and weaken the chemisorption of oxygenated species (14, 15).

While substantial efforts have been exerted to decouple the mechanical and chemical factors in macroscale corrosion phenomena (16), little is known about their initial entanglement at the nanoscale to atomic scale. For the technologically important Ni-Al alloys, attempts have been made to determine the atomic structure of ultrathin surface layer formed on β-NiAl under ideal conditions (17, 18). Recent studies have shown that strain-mediated ionic transport can enhance the oxidation of metal nanoparticles (19), and in situ studies have revealed the critical role of surface defects during the initial oxidation of alloys (20–22). However, a full picture of the atomic-scale processes during gas-metal reactions including possible strain-coupled mechanisms has yet to be reported.

Here, we use in situ atomic-scale environmental transmission electron microscopy (ETEM) to visualize the structural and phase evolution on a single-crystalline Ni–5 atomic % (at %) Al (Al1 phase) surface at 350°C, showing a typical gas-metal reaction pathway from initial surface dynamics to bulk phase change accompanied by chemical-mechanical coupling. Comparative studies demonstrate that different oxidizing agents (O\textsubscript{2} and H\textsubscript{2}O vapor) lead to distinctive atomic mechanisms of oxide growth and kinetics, where the evolving interfacial dynamics plays a substantial role. The experimental observation is corroborated by density functional theory (DFT) calculations and simulations, providing unprecedented atomic insight into the unique role of water vapor in modifying the structures of growing oxides and interfacial structure during oxidation.

RESULTS AND DISCUSSION
Distinct atomic processes for initial oxidation of Ni-Al alloy in O\textsubscript{2} and H\textsubscript{2}O vapor
Figure 1 shows the in situ atomic-scale observations of the onset of oxidation process from a clean Ni-Al (110) surface in O\textsubscript{2} and H\textsubscript{2}O (1 × 10\textsuperscript{−6} mbar) at 350°C, respectively, via high-resolution TEM (HRTEM). In O\textsubscript{2}, the oxidation proceeds through a “step-edge” growth mechanism, i.e., step edges on the alloy surface are the primary source of reacting metal atoms that enable nucleation and growth of oxide islands as indicated by ledge migration (white arrows in Fig. 1, A and B). An energy barrier exists at the oxide-alloy interface, inhibiting O subsurface diffusion to form a “subsurface” oxide (20). As a consequence, the alloy surface atoms are peeled off “layer by layer” as the oxide islands only grow on top of an intact surface. In direct contrast, the oxidation in H\textsubscript{2}O vapor under the same conditions exhibits a direct subsurface growth mode (Fig. 1, C and D), i.e., oxide islands grow into the alloy surface (yellow dashed lines), absorbing adjacent metal atoms to sustain inward...
oxide growth. This growth model indicates that the oxide-alloy interface does not prohibit subsurface diffusion, enabling a direct “attack” to the pristine alloy material by advancing oxidizing species. In the regime of initial oxidation, an increased oxidation rate is also found for the oxidation in H2O by comparing the consumed atomic layers of alloy substrates in Fig. 1 (A and C). These observations demonstrate different atomistic processes for initial alloy oxidation under O2 and H2O gas environment.

Changing oxidizing species from O2 to H2O introduces adsorbed hydroxyl through water dissociation, and OH can further dissociate into atomic H and atomic O, where atomic O serves as oxidizing agents (23). It may be argued that, associated with the charge transfer between Ni and Al (24), alloying of Ni with Al could possibly change the surface adsorption behavior. However, the oxidation process is thermodynamically dominated by the oxide formation energy, therefore making the alloying effect less important, especially for the case of a dilute solid solution of ~5 at % Al. The initial oxide formed on dilute Ni alloys has been reported to be NiO (25–29) before possible alloying elements (e.g., Cr and Al) incorporated into the oxides, which is in accordance with the results of our phase identification based on lattice imaging and the subsequent analysis as detailed in fig. S2. To understand the oxidation reaction mechanisms in H2O, we use DFT and ab initio molecular dynamics (AIMD) calculations to elucidate the possible effect of dissociated H2O molecules on oxide formation at a preexisted NiO/Ni interface. The major difference between the oxidation by O2 and H2O lies in the existence of H in...
the case of H$_2$O. Hence, our simulation focuses on the response of the preformed oxide to H. As shown in Fig. 2, a pyramid-shaped NiO is built on Ni surface according to experimental observations in Fig. 1. Two views of the relaxed NiO/Ni interface are illustrated in Fig. 2 (A and B), where seven Ni (002) atomic layers match with six NiO (002) atomic layers according to their lattice misfit. To simulate the oxide growth process in a water vapor environment, we introduce preadsorbed H atoms and OH groups to the surface of the relaxed structures in Fig. 2 (A and B). As shown in Fig. 2 (C and D), after 10 ps, the NiO became defected, and Ni and O atoms in the oxide became disordered, which shows a clear perturbation on the growing oxide brought by H atoms. For initial oxide embryo nucleation and growth, it usually has a metastable atomic structure due to its small size (<2 nm); hence, the H can easily affect the stoichiometric growth of the oxide as evidenced by HRTEM imaging (Fig. 1). At the same time, H is found to diffuse from the adsorption surface to the oxide-alloy interface (Fig. 2D). It is well known that H can easily diffuse through oxides via interstitial sites with a small diffusion barrier (29, 30); hence, we usually do not expect H to aggregate at specific sites. As shown by the simulation results, the interfacial enrichment of H indicates that the oxide-alloy interface acts as an energetically favorable “sink” for H ions. This is critical for understanding distinct growth mechanisms between dry oxidation and oxidation by water vapor observed in Fig. 1. Specifically, the H generated from water dissociation diffuses to the oxide-alloy interface, which could lead to the destabilization of the oxide-alloy interface, as shown

Fig. 3. Strain-mediated Ni-Al oxidation by O$_2$ and H$_2$O. Time-lapse HRTEM images demonstrate atomic-scale cross-sectional view of strain-mediated alloy oxidation process (1×10$^{-4}$ mbar and 350°C) on the Ni-Al surface. (A) Oxidation in O$_2$ initiates from surface oxide islands (white arrows; 6 s) to inward oxide growth into the alloy substrate (the interface indicated by white dashed lines; 73 s) and forms a highly strained dislocation zone (between yellow and white dashed lines; 100 s). (B) Oxidation in H$_2$O initiates from surface oxide islands (30 s) to inward oxide growth into the alloy substrate (the interface indicated by white dashed lines; 42 and 64 s), but the growing interface is absent of dislocation zone compared with that in O$_2$. (C) HRTEM image shows four zones at the growing oxide-alloy interface in O$_2$, from the surface to bulk: 1. Surface oxide; 2. Bulk NiO; 3. Dislocation zone (the interfacial area between oxide and substrate); 4. Alloy substrate, as illustrated by the atomic structure model. (D) HRTEM image shows only two zones presented at the growing oxide-alloy interface in H$_2$O: 1. Oxide (less ordered) and 4. Alloy substrate, as illustrated by the atomic structure model. Scale bars, 2 nm (A) and 1 nm (B to D).
by the direct attack to the alloy substrate in Fig. 1 (C and D). It should be noted that upon adsorption and dissociation process of gas molecules on metal surface, it takes a time scale of several seconds to initiate the oxidation reaction. Therefore, there is a gap in the time scale between the molecular dynamics simulation of several picoseconds and the experimentally observed surface reaction of several seconds. Apparently, the picosecond simulation reveals a snapshot of the dynamics of the whole system. These combined experimental and theoretical results reveal a possible effect of water vapor on the initial stages of oxide formation. It is, however, intriguing to also consider how water vapor affects later stages of the oxidation process.

**Metal-oxide interface structure and its effect on oxidation of Ni-Al alloy in O$_2$ and H$_2$O**

The atomic-scale transitions of the oxidation process from initial oxide nucleation to bulk growth in O$_2$ and H$_2$O at a higher pressure ($1 \times 10^{-4}$ mbar) at 350°C are depicted in Fig. 3 (A and B, respectively). Although the oxide growth on a clean NiAl (110) surface features similar stages for the two different gas environments (i.e., proceeding from the formation of metastable surface oxides to coalescence of these surface oxides and subsequent inward oxide growth), the oxidation by O$_2$ (Fig. 3A) exhibits a highly strained interface (white dashed lines) between oxide and alloy, propagating into the alloy and forming a dislocation zone (between white and yellow dashed lines). On the contrary, the oxidation by H$_2$O vapor exhibits neither lattice distortion nor dislocation formation. Instead, a disordered oxide and incoherent interface between oxide and alloy accommodates the lattice mismatch. While the breakdown of the step-edge growth mechanism in O$_2$ is due to a higher chemical potential for the oxidation reaction at a higher gas pressure, the lattice mismatch-induced strain at the coherent alloy-oxide interface contrasts that in H$_2$O with a non-coherent interface, as shown in Fig. 3 (C and D). In Fig. 3C, a dislocation zone, and alloy substrate as sequentially labeled as zones 1 to 4. In direct contrast, the interfacial region formed in H$_2$O lacks both a distinct dislocation zone and a zone of well-ordered epitaxial NiO, as shown in Fig. 3D. Detailed analysis of the oxide-alloy interface formed in O$_2$ finds that six layers of oxide lattice correspond to seven layers of alloy lattice, which is in accordance with the lattice mismatch (16.67%) between cubic NiO ($\alpha = 3.575$ Å) and face-centered cubic Ni–10 at % Al ($\alpha = 3.575$ Å) (fig. S3A). It also finds that the interfacial strain is reduced from 16.67 to 11.76% through the incoherent interface formed in H$_2$O (fig. S3B). It needs to be mentioned that the Moiré patterns shown on the alloy substrate lattice in Fig. 3 (B and D) were due to the surface oxide formation on the Ni-Al (100) surface (the projection view), as shown in fig. S4.

As shown above, the formation of the strained interface during inward/bulk oxidation requires extra energy for the proceeding of oxidation reaction, which became the dominating factor in the oxide growth in O$_2$. In the oxidation by H$_2$O, this strained interface is relaxed by forming an incoherent interface between the oxide and alloy substrate in H$_2$O. Strain mapping based on the in situ HRTEM observation confirms that considerable strain accumulated at the interface between oxide and alloy substrate for the oxidation by O$_2$ (Fig. 4, A and B), while a relatively mild and uniform strain distribution is shown for the oxidation by H$_2$O (Fig. 4, C and D). These different strain levels have an immediate impact on the following growth kinetics. In Fig. 4E, we tentatively quantify the oxide growth rate in two environments by comparatively counting the oxide layers formed in a period of time. By real-time HRTEM imaging, we could also differentiate the “outward oxidation,” which means the addition of surface oxide layer to the initial alloy surface, from the “inward oxidation,” which means that the oxide forms by incorporating oxygen atoms into or below the initial alloy substrate. The former case is dominated by surface diffusion of O and metal atoms, while the latter case is dominated by diffusion of O to the alloy-oxide interface. Assuming a uniform growth of oxide, a faster inward oxidation is seen for the oxidation by H$_2$O comparing with that by O$_2$, while no noticeable difference is observed for outward oxidation between two cases as seen in Fig. 4E, where a clear enhanced inward oxidation in H$_2$O is seen.

**CONCLUSION**

In summary, early stages of atomic-scale oxidation process are captured on Ni-Al surface by in situ ETEM. As the oxidation proceeds from the surface to the bulk alloy, the nature of the interface between oxide and alloy governs the atomistic processes and oxidation mechanisms. In O$_2$, a nearly coherent highly strained interface inhibits...
subsurface diffusion of O, which leads to a step-edge mechanism at lower pressures and keeps imposing an energy barrier to retard the oxidation reaction at higher pressures. On the contrary, oxidation in H₂O shows a direct subsurface mechanism with an enhanced oxidation rate at both lower and higher pressures compared with that in O₂. DFT calculation and simulation reveal the role of dissociated H₂O in this strain-coupled oxidation reaction as a structural interrupter and ion diffusion enhancer. These results clarified the atomistic mechanisms of initial oxidation and provide insights into other strain-mediated chemical reactions.

MATERIALS AND METHODS

Ni-Al alloy thin-film deposition
Single-crystalline Ni-Al alloy of 50-nm-thick thin film was deposited on a NaCl substrate at 400°C using a dual-beam electron-beam evaporation system. The concentration of each element was controlled through individual evaporation rate (9.5 Å/s for Ni versus 0.5 Å/s for Al), resulting in an atomic ratio of ~5% of Al in the Ni-Al alloy films confirmed by energy-dispersive x-ray spectroscopy analysis. Following deposition, the NaCl substrate was removed by water dissolution, and the as-deposited alloy thin films were confirmed to be single crystal via electron diffraction.

ETEM oxidation experiments of Ni-Al alloy
An FEI Titan ETEM equipped with an objective lens aberration corrector was used for Ni-Al oxidation experiments. The single-crystalline (100) Ni-5% at% Al alloy thin films were prepared by washing in acetone and methanol several times and mounted on a holey silicon TEM grid for observation. A partial pressure up to a few millibars can be reached in the ETEM and at a temperature up to 850°C can be reached by a Gatan 652 double-tilt heating holder. Before oxidation, the alloy thin films were annealed at 700°C in a high vacuum of <1 × 10⁻⁸ mbar (fig. S1), resulting in a clean surface. Pure oxygen (~99.999%) was introduced into the TEM column through a leak valve to oxidize the thin films at a given temperature and pressure. For oxidation in water vapor, the water vapor was generated and delivered to the ETEM column by a water vapor system (29) developed in-house. The gas pressure can be adjusted from 1 × 10⁻⁸ to 15 mbar. The electron beam dose rate was chosen as ~5 × 10⁻⁶ e·nm⁻²·s⁻¹ on the basis of calibrations of the electron beam effect according to the established methods (detailed in the Supplementary Materials).

Strain analysis of HRTEM images
The strain analysis of the time-resolved HRTEM image is conducted by DigitalMicrograph software with a geometric phase analysis in FRWRtools plugins.

Computational methods
The Vienna Abinitio Simulation Package (VASP) (31, 32) was used to perform DFT and AIMD calculations to model the NiO/Ni interface geometry and structural evolution in the presence of dissociated H₂O molecules. Projector augmented wave (PAW) (33) atomic pseudopotentials were used to describe the potentials of nuclei and core electrons. The generalized gradient approximation with the parameterization of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation functional (34). The on-site coulomb interaction of the 3d electrons of Ni in NiO was accounted for by adding a Hubbard-U term (35), with a U value of 5.3 eV (36). The lattice parameters of Ni and NiO were calculated to be 3.51 and 4.20 Å, respectively. The NiO island was modeled as pyramid shape to mimic experimental observation. Previous theoretical work showed that the NiO (100) surface is the most stable among all low-index NiO surfaces (37), so the termination of the NiO island parallel to the substrate was chosen as (100). To construct a periodic simulation cell and minimize the strain of NiO oxide, the NiO/Ni interface was modeled with six repetitions of Ni unit cell and five repetitions of NiO unit cell, both along the [100] direction (Fig. 4).

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