Scalable Variable Charge Molecular Dynamics Simulations of Metal-Oxide Systems

Gabriel Plummer, Jacob Tavenner, Mikhail Mendelev, John Lawson

NASA Ames Research Center

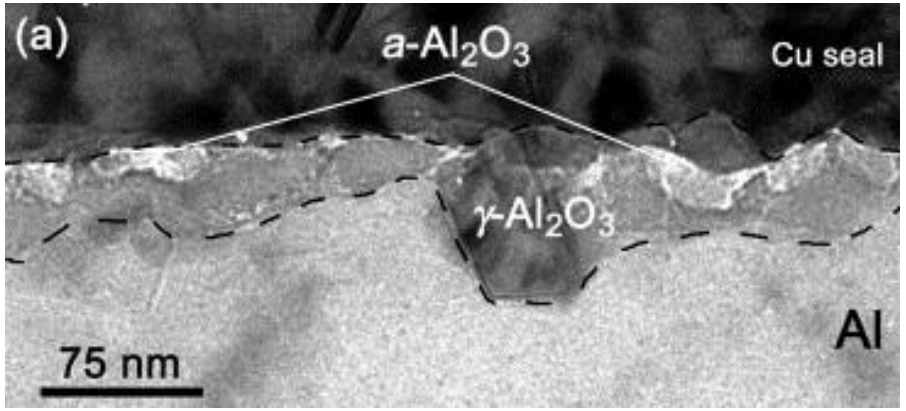
Acknowledgements

- NASA Glenn Research Center
  - Tim Smith

NASA Aeronautics Research Mission Directorate (ARMD) Transformational Tools and Technologies (TTT) Project

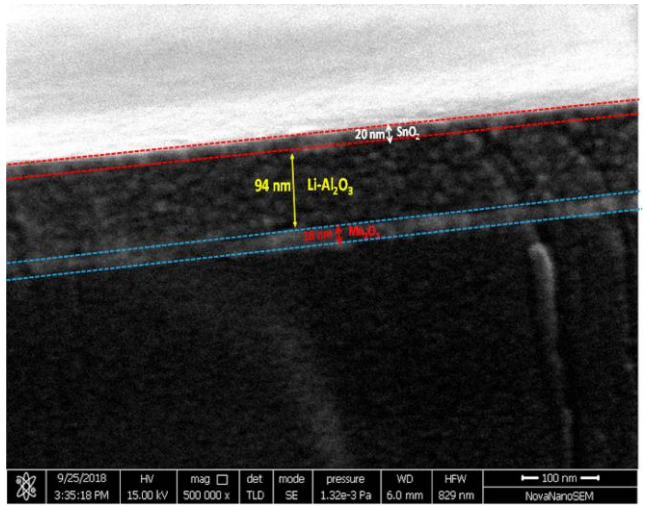
Importance of metal-oxide interfaces

Surface oxidation



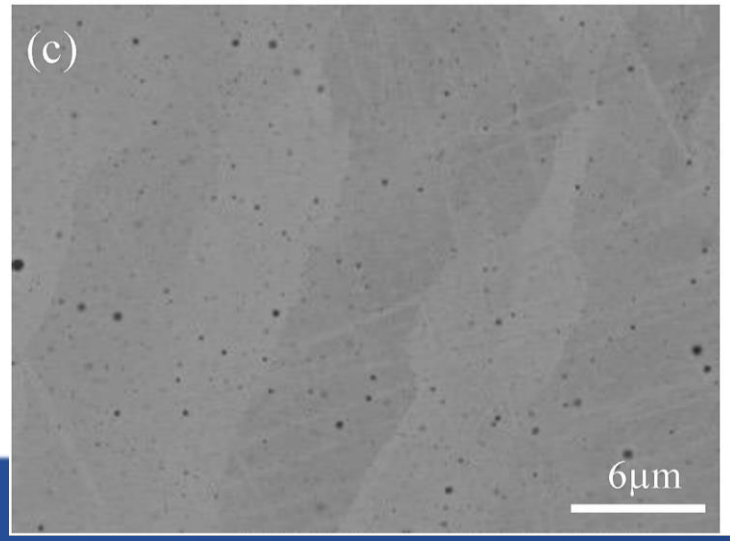
L.P.H. Jeurgens et al., *Thin Solid Films* 418, 89 (2002)

Dielectric components



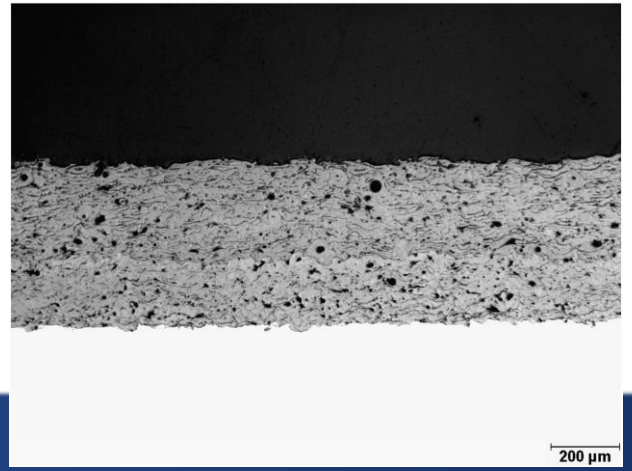
N. Pal et al., *ACS App. Electronic Materials* 2, 25 (2020)

ODS alloys



C. Qiu, *J. Alloys and Compounds* 790, 1023 (2019)

Thermal barrier coatings



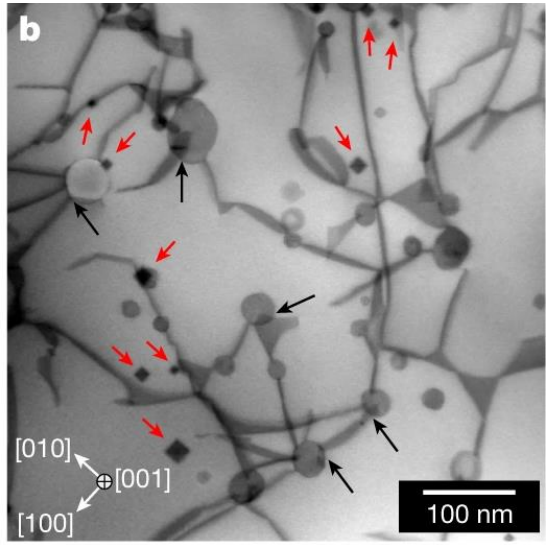
R. Vassen et al., *Surface and Coatings Tech.* 205, 938 (2010).

NASA motivation

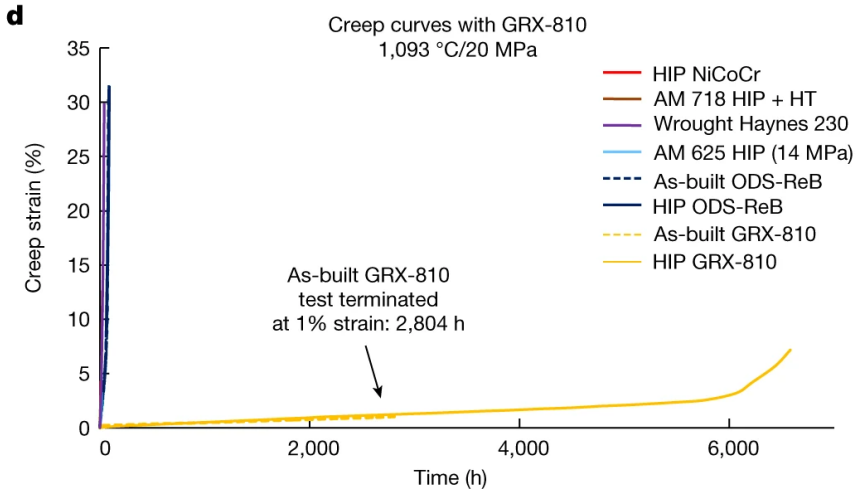
A 3D printable alloy designed for extreme environments

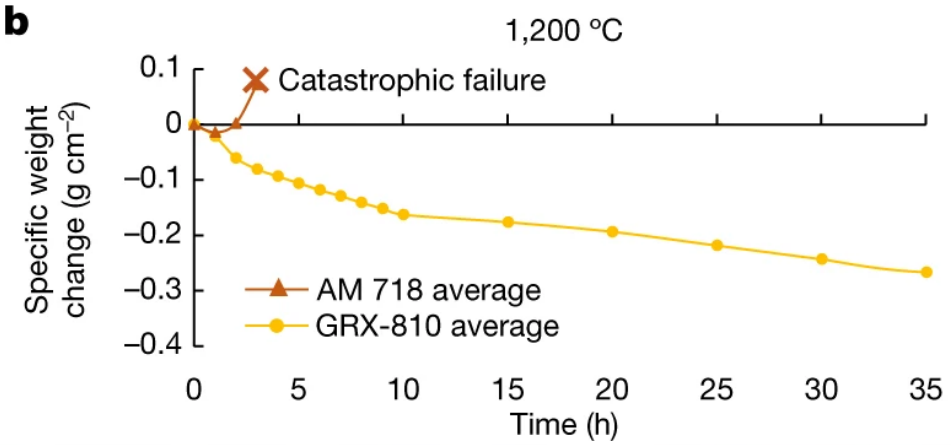
Timothy M. Smith, Christopher A. Kantzos, Nikolai A. Zarkevich, Bryan J. Harder, Milan Heczko, Paul R. Gradl, Aaron C. Thompson, Michael J. Mills, Timothy P. Gabb & John W. Lawson

Nature **617**, 513–518 (2023) | Cite this article



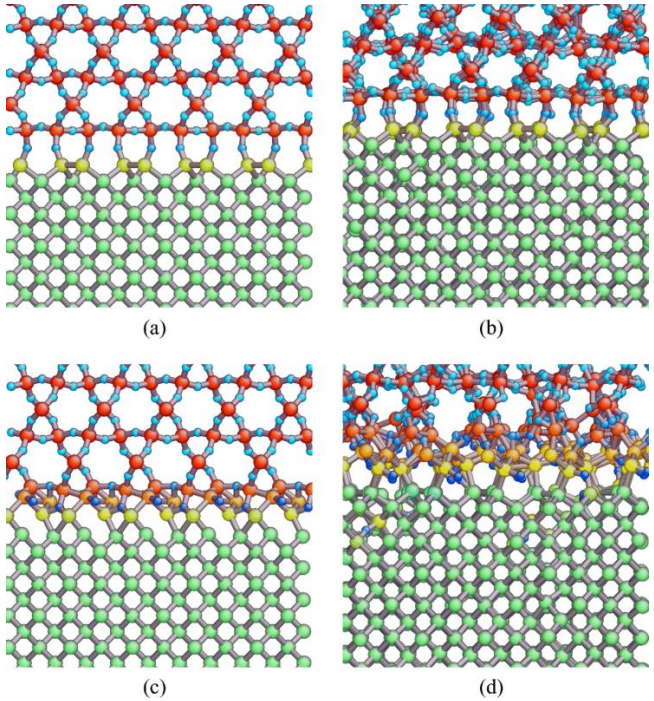
GRX-810 is a novel ODS alloy with unprecedented creep and oxidation resistance





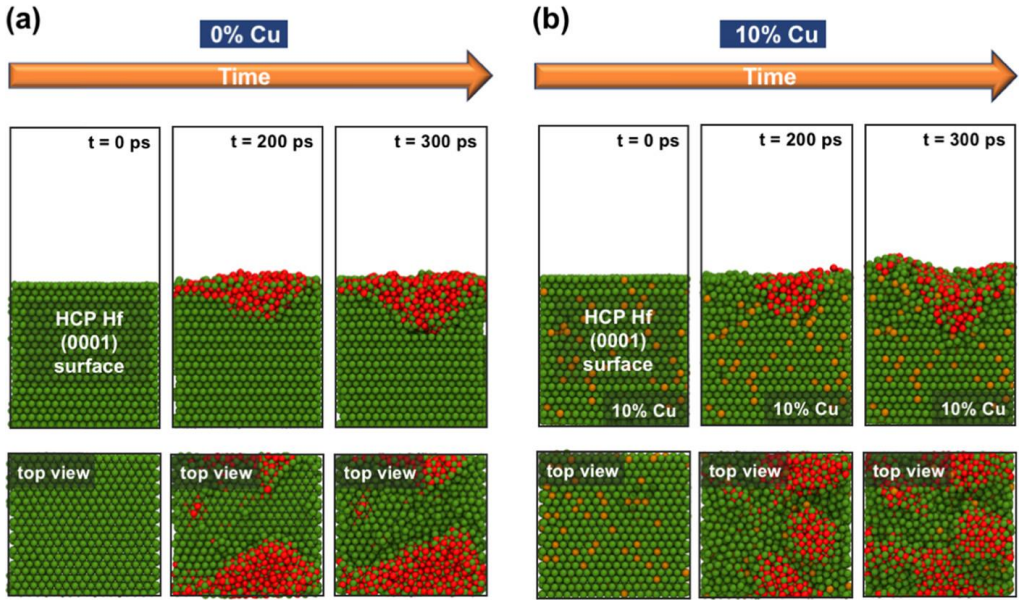
Usefulness of MD simulations

Determination of interfacial structures



E. Lee et al., *Phys. Rev. B* 93, 144110 (2016)

Simulation of atomic-scale mechanisms



K. Sasikumar et al., *Chem. Mater.* 31, 3089 (2019).

MD simulations of metal-oxide systems require specialized interatomic potentials to accurately describe the heterogeneous bonding.

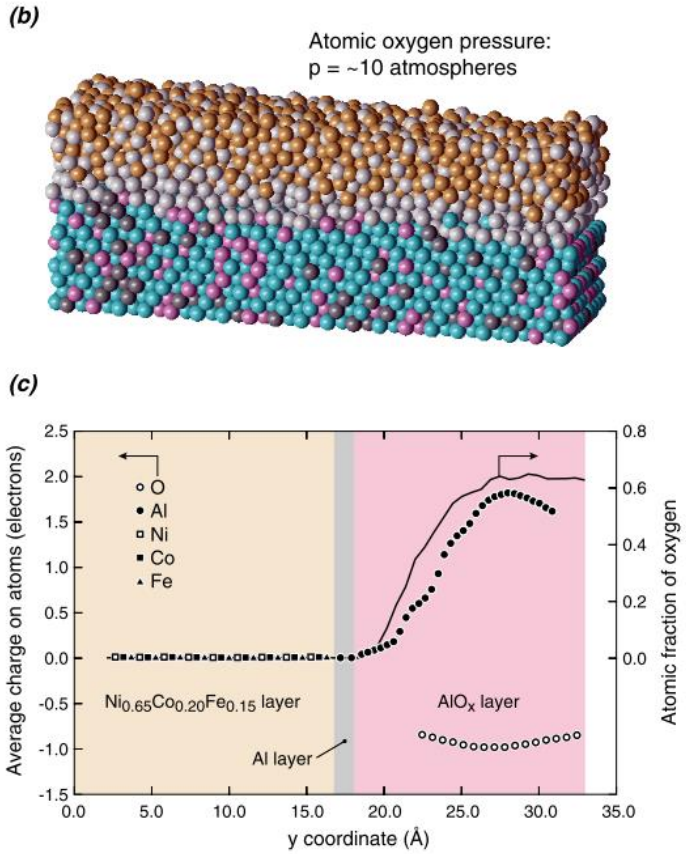
Overview

- Brief intro to simulation methodology

- 2 case studies for the Ni-O system
  - Surface oxidation
  - Dislocation-oxide interactions

Variable charge MD

Charge profile develops across interfaces



- System energy partitioned into ionic and non-ionic components:

$$E_{total} = E_{ionic} + E_{non-ionic}$$

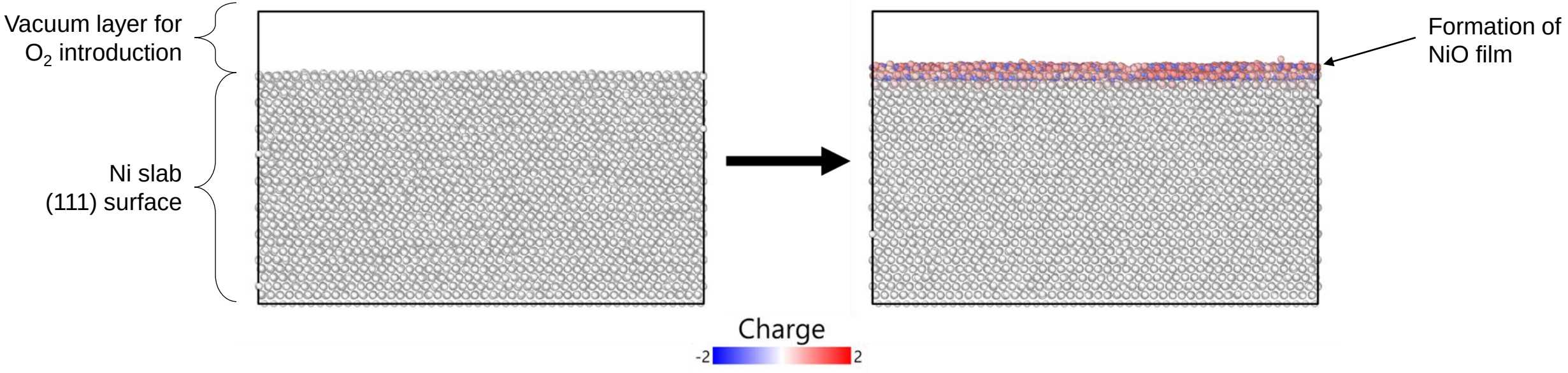
- Stages in each MD step:
  1. Obtain equilibrium atomic charges based on energy minimization algorithm
  2. Get atomic forces based on interatomic potential
  3. Advance atomic positions

- Step 1 makes variable charge MD expensive – we have introduced efficiency improvements:
  - Replacement of the traditional Ewald summation for ionic interactions with an equivalent damped, shifted potential. Scaling improves from ***NlogN*** to ***N***.
  - Charge equilibration can be applied to only a small subset of atoms in the system, i.e., those close to an interface.
  - These improvements have been implemented in the widely available LAMMPS package.

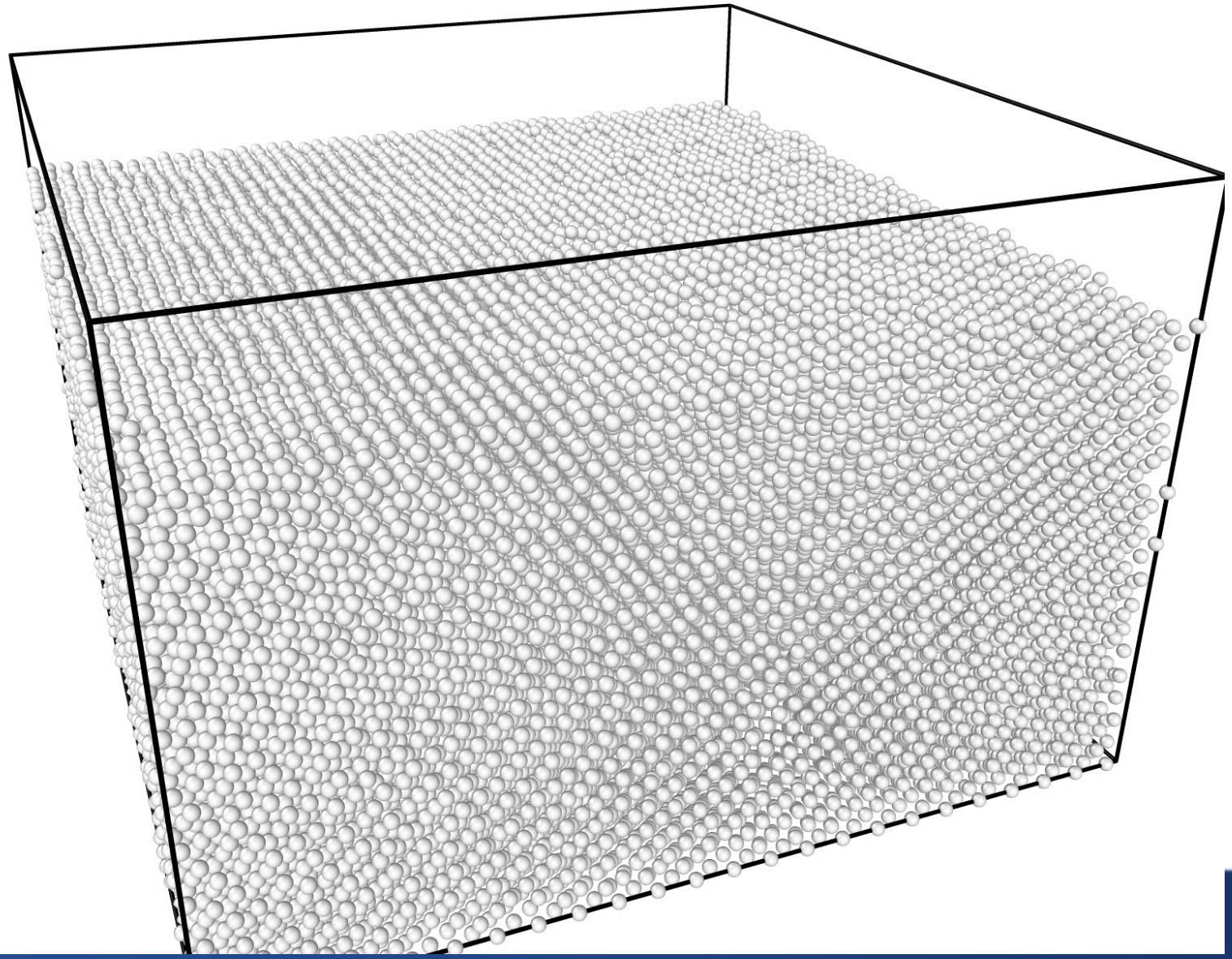
X.W. Zhou and H.N.G. Wadley, *J. Phys.: Condens. Matter* 17, 3619 (2005)

Ni Surface Oxidation

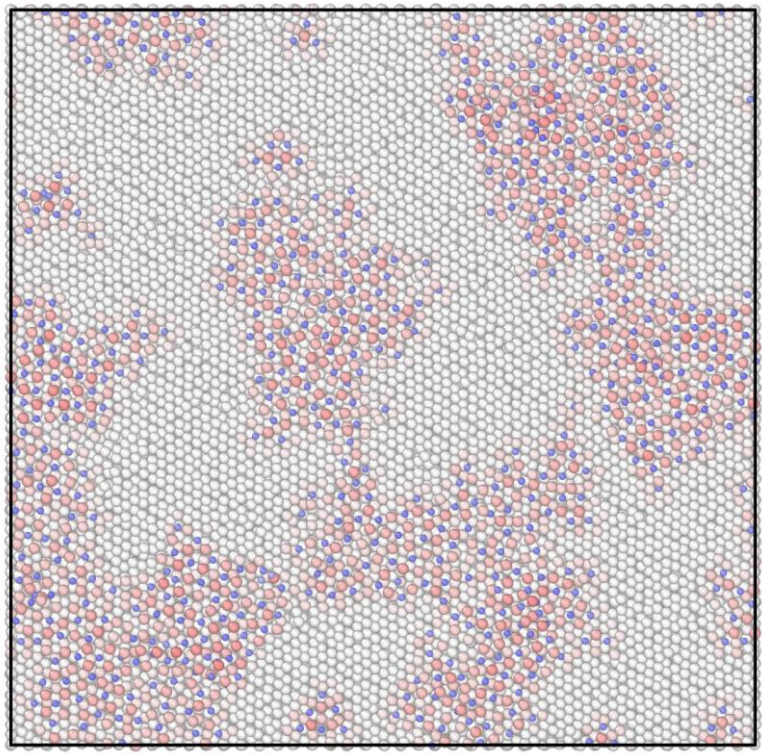
Simulation setup



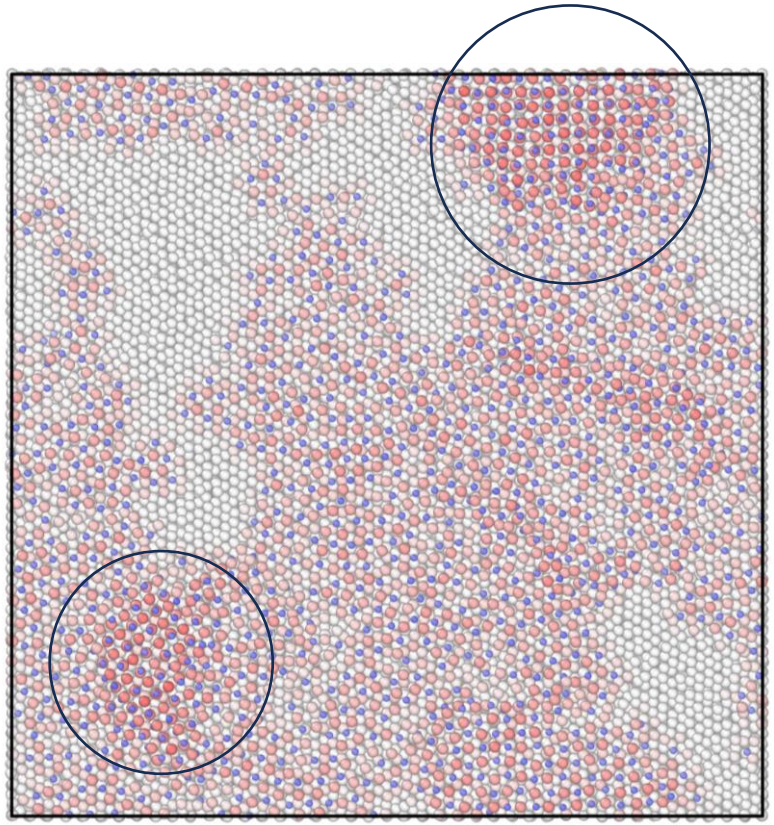
Oxidation at 800 K



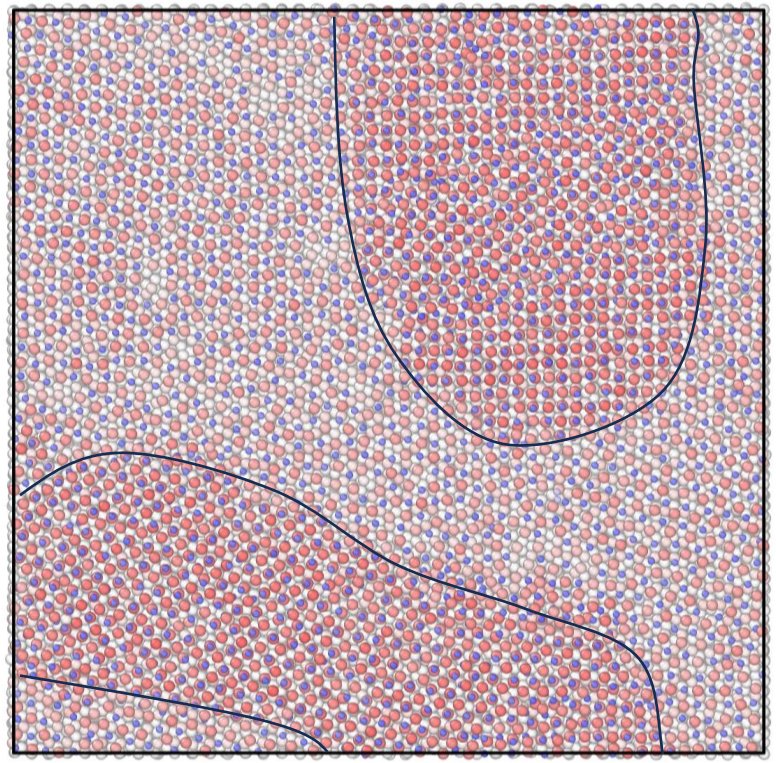
Mechanisms of oxide film formation



Initial stage of dissociation and adsorption

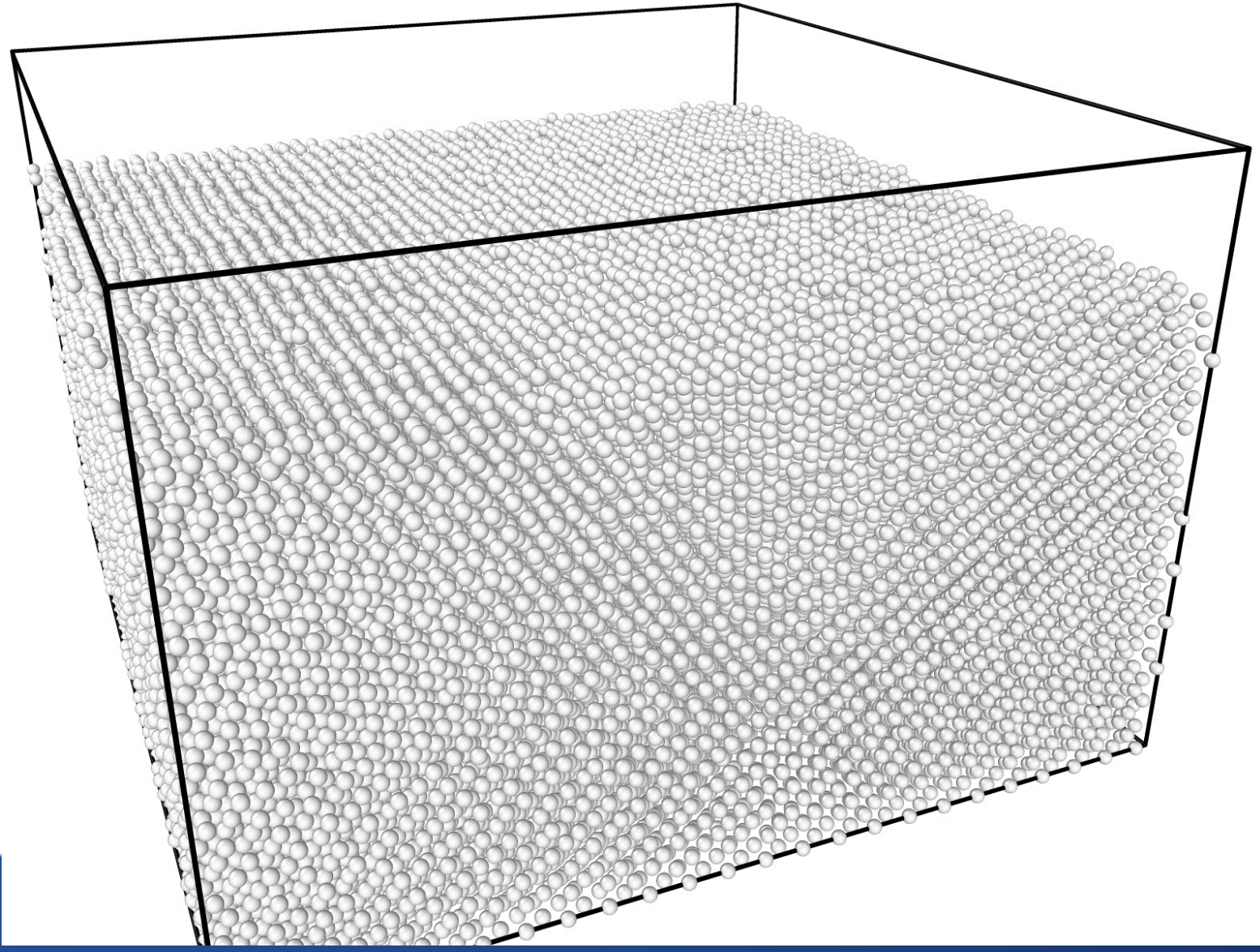


Nucleation of ordered oxide regions

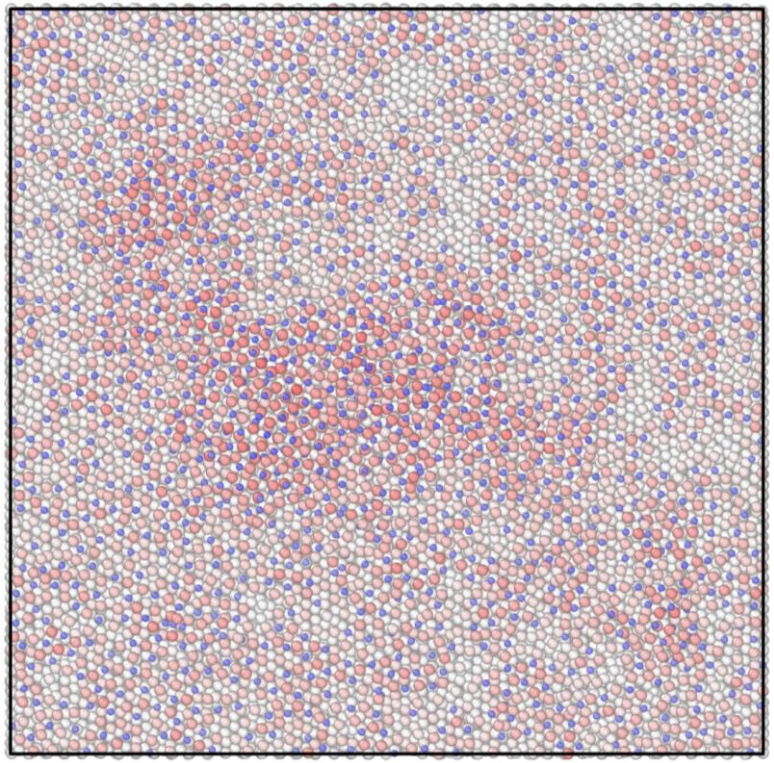


Planar growth of oxide across surface

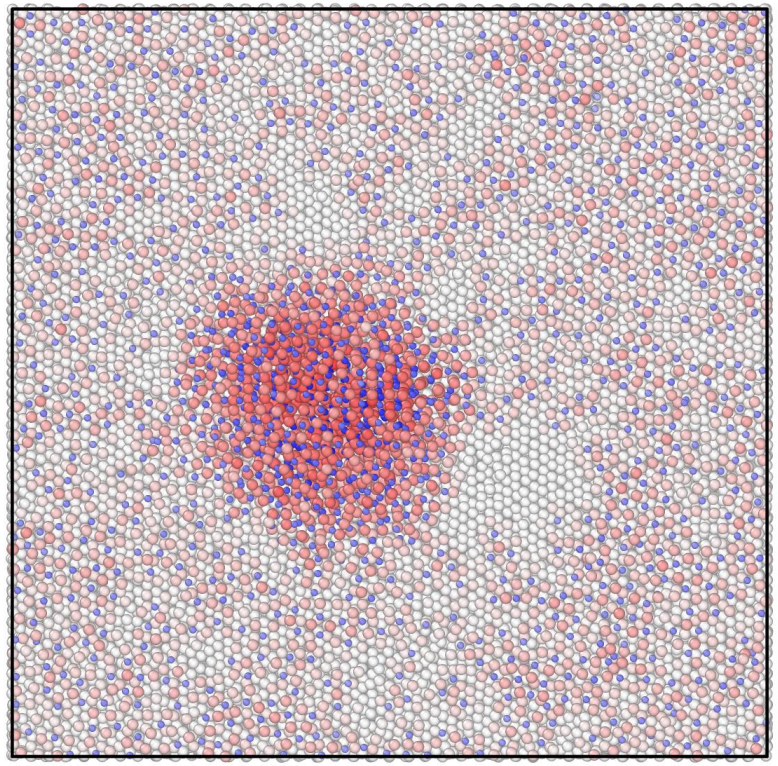
Increasing temperature to 1000 K



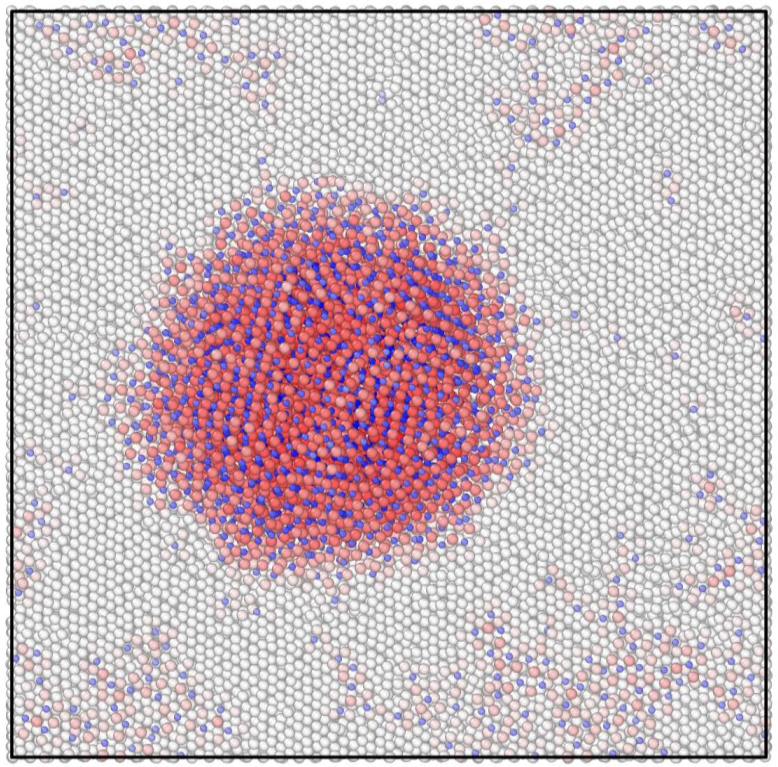
New mechanism activated



Initial stage of dissociation and adsorption



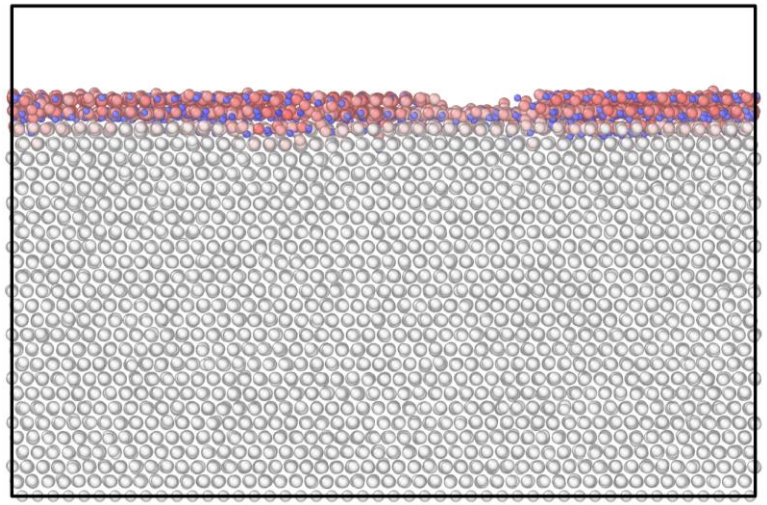
Nucleation of large oxide island



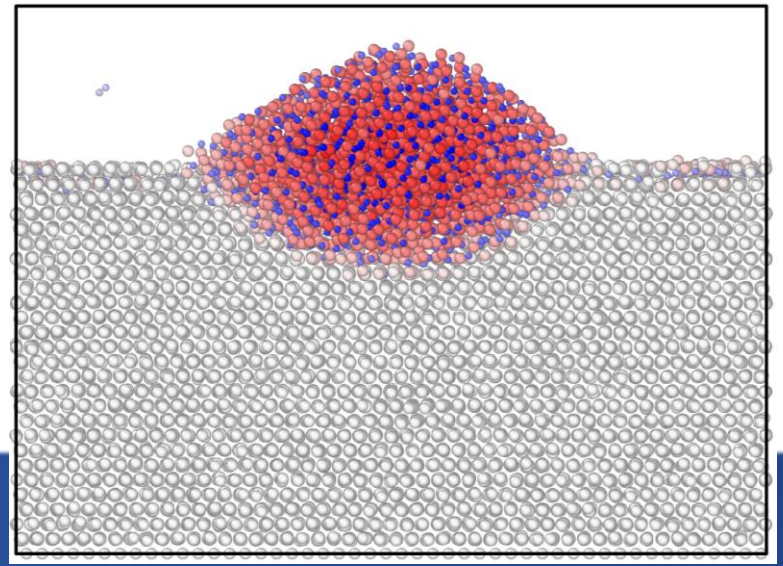
Lateral and vertical growth of oxide island

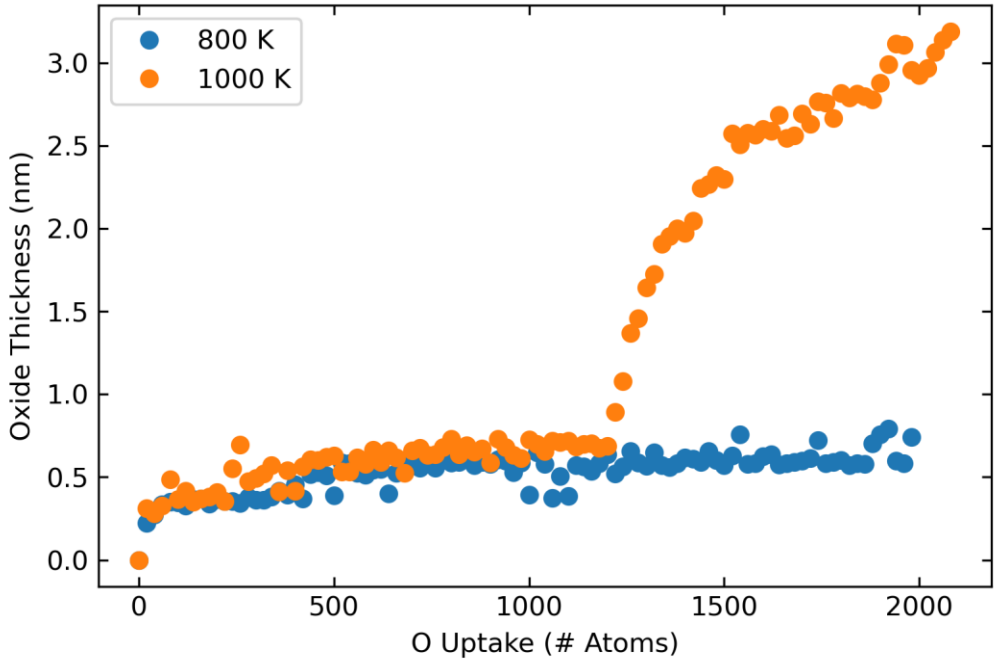
Accelerated oxide growth at high T

800 K



1000 K

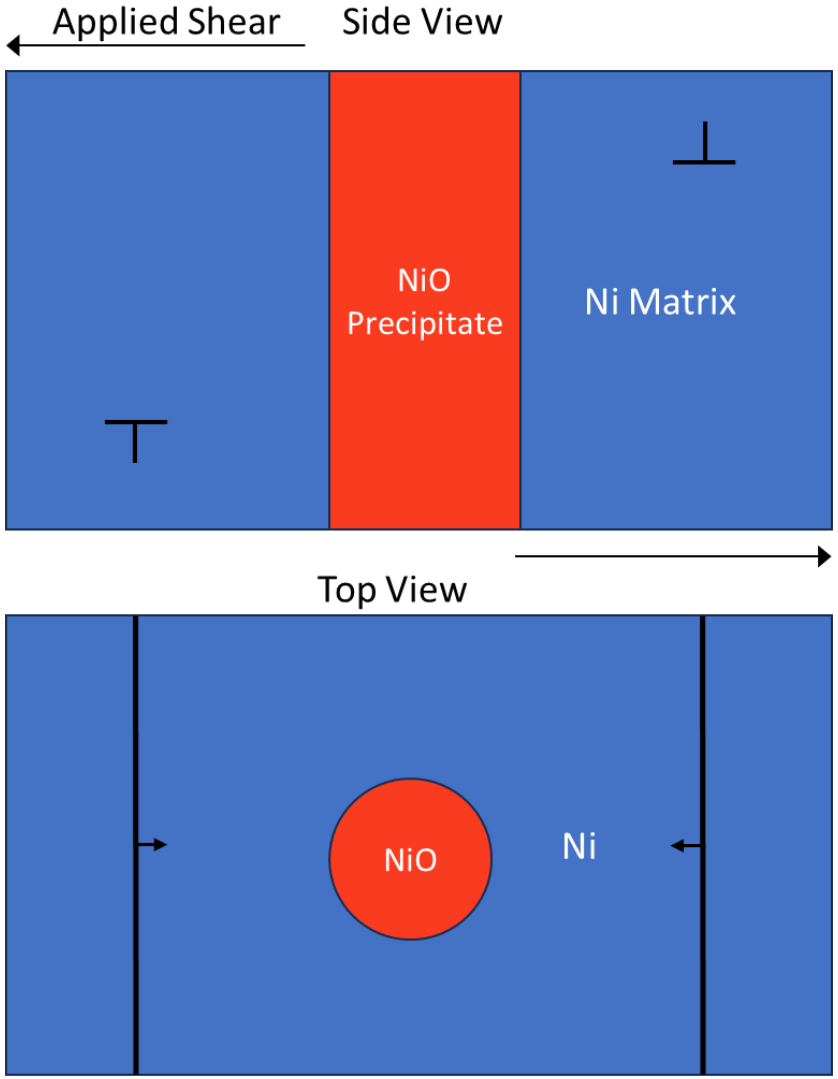




- Oxidation kinetics can be connected to atomic-scale mechanisms with MD simulations.
- Long MD time scales (20-30 ns) were required to observe the relevant mechanisms.

Dislocation Interactions with NiO

Simulation setup

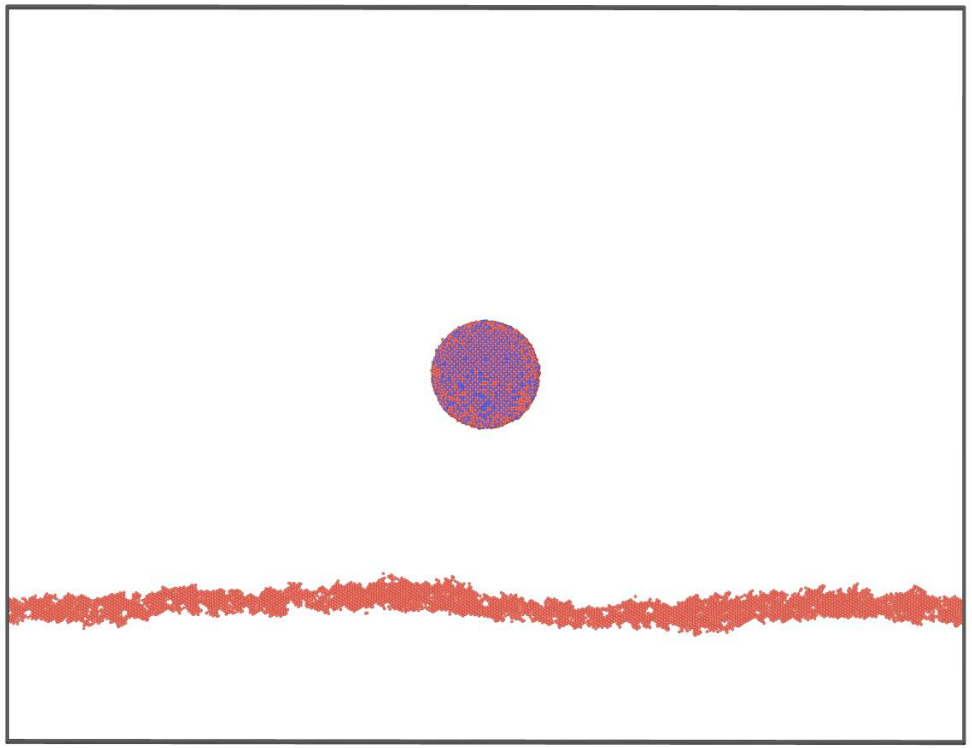


- Dislocations inserted in an FCC Ni matrix
- NiO particle inserted as an obstacle
- Apply shear stress at 1000 K

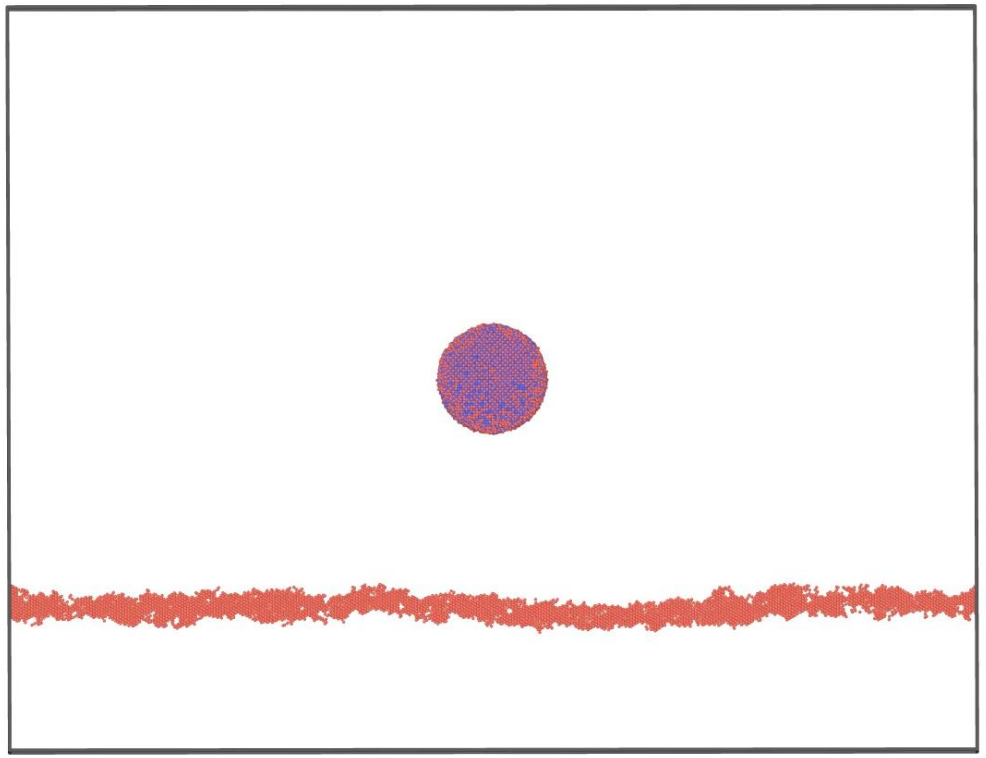
⊥ : Dislocation

ODS mechanism observed

100 MPa

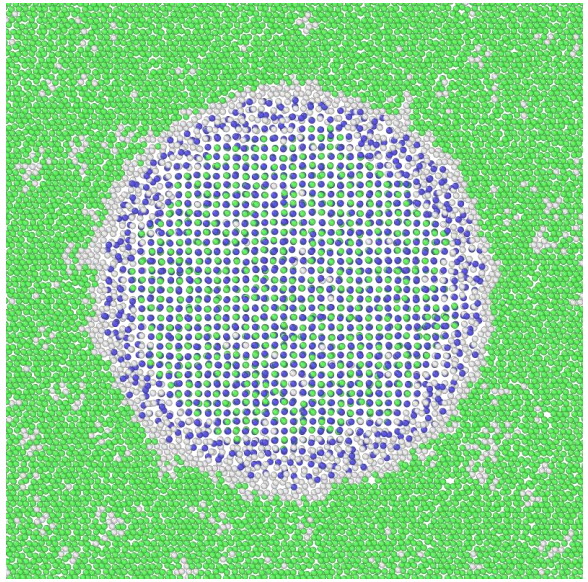


200 MPa



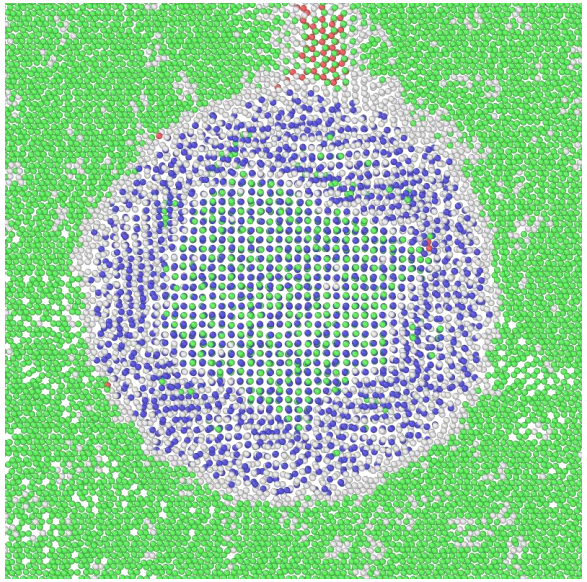
Interfacial region is key

Initial thin amorphous interfacial region



Dislocation bypass

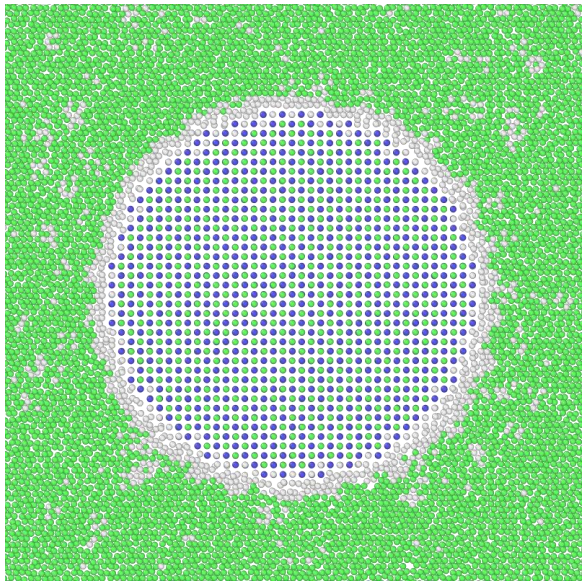
Deformation accommodated at interface



Ni atoms colored by structure: FCC – green, HCP – red, Other – white

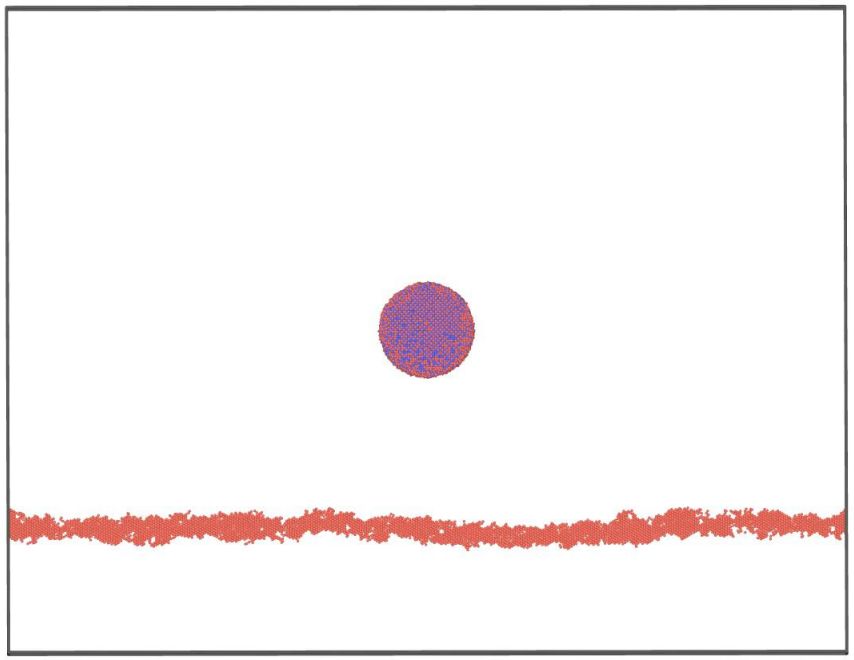
O Atoms colored Blue

What happens if we fix the interfacial region to be crystalline and atomically sharp?

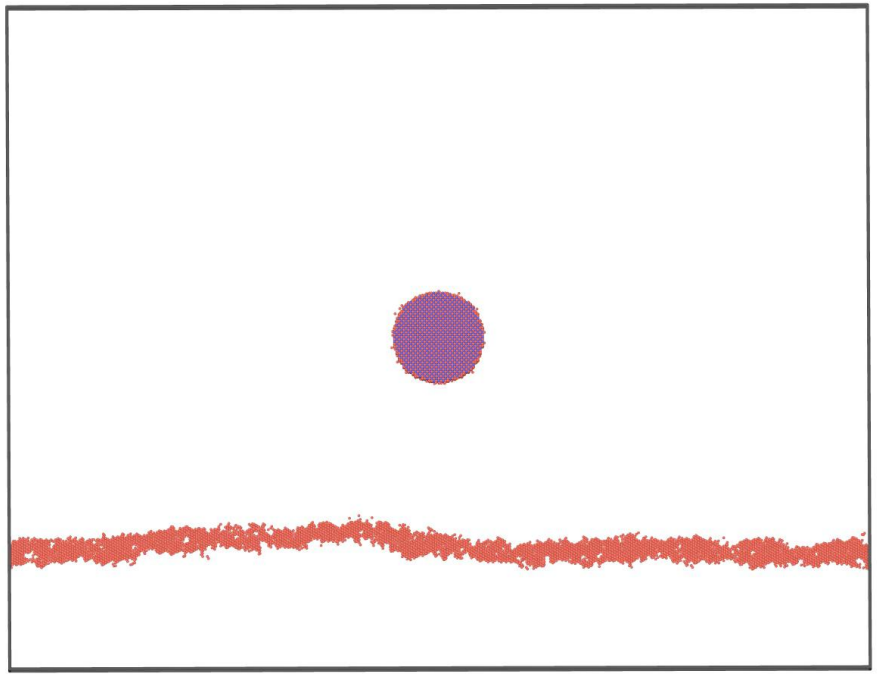


Greater strengthening with fixed interface

Amorphous interface – 200 MPa



Fixed interface – 200 MPa



- ODS behavior is connected to atomic-scale structure of metal-oxide interfaces.
- Large scale (> 10 million atoms) simulation enabled by limiting variable charges to region surrounding NiO

Summary

- Metal-oxide interfaces are an important feature in many technologically relevant materials
- Specialized MD simulation techniques have been developed to accurately model these interfaces at the atomic-scale
- Atomic-scale mechanisms and structures can be connected to key material properties