

## Multiscale vacancy and dislocation-mediated surface segregation in CuNi alloy up to microsecond timescales with accelerated dynamics

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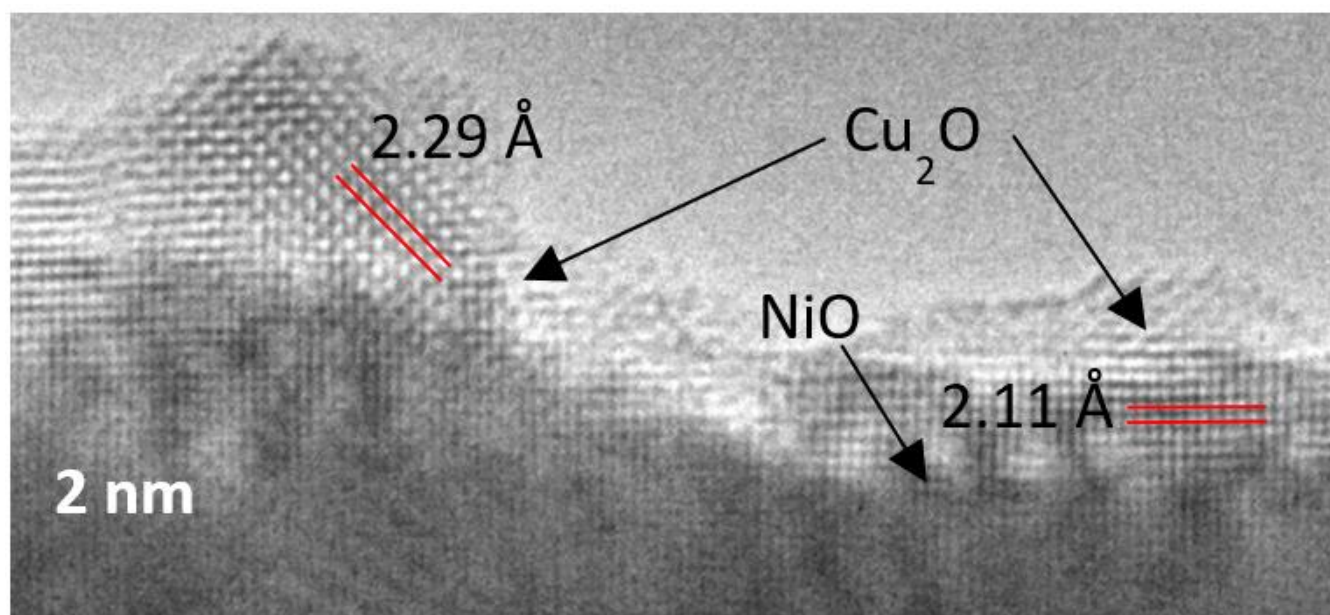
Phase separation of CuNi in vacuum is well-documented in both theory and experiment: annealing enriches the exposed surfaces with Cu and the subsurface layers with Ni [1, 2]. Even before exposure to air or corrosive environments, the bimetal restructures, affecting outcomes in both oxidation and reduction experiments. Transformations on the atomic and nanoscale could influence the study of Cu-Ni catalysts e.g. for the reduction of CO<sub>2</sub>, as well as in corrosion-resistant, marine alloys, making it difficult to replicate behavior between samples observed using microscopy techniques. Fig. 1 is an image taken during HRTEM observation and in situ oxidation of CuNi(100): the metals are impossible to distinguish within the alloy, since they display low lattice mismatch, and their oxides also exhibit little difference in d-spacing. Further, the atomic mechanisms, dynamics, and rate of this restructuring are difficult to observe, since the two metallic nuclei are difficult to distinguish even with Z-contrast, and elemental mapping is only available over long times (minutes to hours). The migration and coalescence of individual vacancies is also poorly resolved in experiment, yet the flow of point defects towards an exposed surface is directly related to the well-known counterflow of Ni into the bulk lattice. Computationally, the atomic transformations underlying nanoscale alloy restructuring are much more effectively resolved using molecular dynamics (MD). However, these only reveal short time scales up to nanoseconds, not the dynamics occurring over microseconds and beyond that are most significant in alloy surface segregation processes approaching experimental times. To address this challenge, we utilize two accelerated methods, ParSplice and Adaptive Kinetic MC (AKMC), to evolve to longer time frames and narrow this gap, comparing our results with standard MD to distinguish surface segregation mechanisms by their different timescales.

We employ an embedded-atom method (EAM) forcefield in our simulations. As a first step, we have validated the accuracy of the potential by comparing to density functional theory (DFT) calculations. Specifically, we calculated the monatomic segregation energy of Ni dopant in pure Cu surfaces (100), (110), and (111). Comparing the DFT surface energies (J/m<sup>2</sup>) of structures with a single Ni atom included at surface, subsurface, and interior layers, respectively, we noted that placing Ni in the bulk is most favorable for the (111) surface, followed by the (100) orientation, behavior illustrated in Fig. 2 (not included to meet 2 figure limit). These tests distinguish the performance of the 2019 EAM potential of Fischer et al as superior to other potentials [3], which we then utilized to obtain the dynamics over longer times with MD (ns) and accelerated MD (μs).

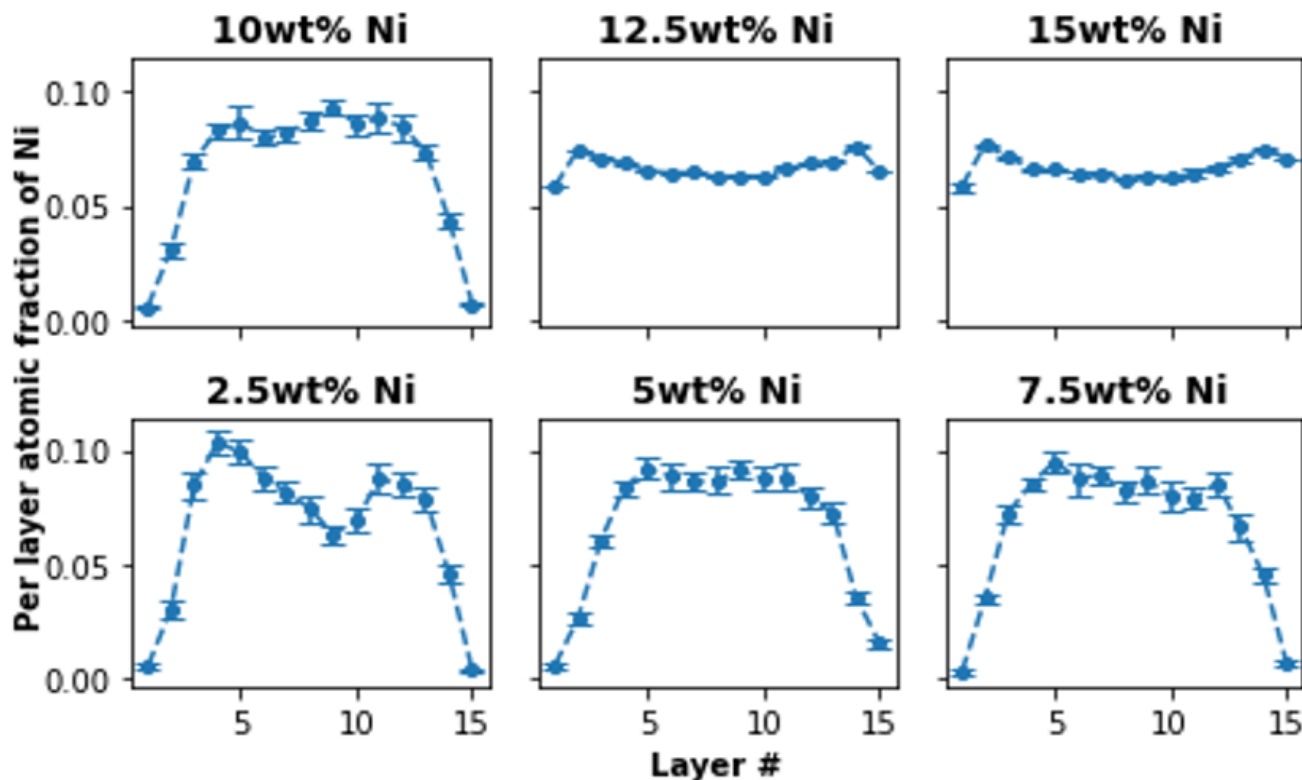
We simulated annealing across a range of temperatures, dopant concentrations, and vacancy concentrations using LAMMPS to perform pure MD and hybrid MD/Monte Carlo (MC). The composition versus layer depth in Fig. 3 displays Ni enrichment in the subsurface and bulk found with MC. Even after 400 ns of MD, we were not able to observe equilibrium profiles. Clearly, slower dynamics will evolve the

states reached in MD to those shown in Fig. 3. To observe these dynamics occurring over several  $\mu\text{s}$ , we employ ParSplice and adaptive kinetic Monte Carlo (AKMC) to carry out accelerated MD [4, 5].

In both pure and accelerated MD, we observe multiple mechanisms of vacancy condensation and percolation to the surface which allow compensating nickel migration into the bulk. By tracking the  $z$ -coordinate of the Ni particles as well as the lattice vacancies, the variance and cross-correlation of the particle trajectories was computed, allowing for Ni segregation into the bulk to be spatially and temporally matched with defect glide towards the exposed CuNi surface. The heatmap in Fig. 4 (not included to meet 2 figure limit) quantifies the strong lead-lag relationship between one point defect and a single nickel atom at 600 K, a brief spike in cross-correlation lasting for dozens of picoseconds. The leader-follower dynamic between vacancy and nickel atom is similar for multiple nearby vacancies as well, showing that their movement precedes monoatomic Ni segregation by fractions of a nanosecond. Though neighboring copper atoms have trajectories correlated with this segregation event, we show that the relationship is stronger with the vacancies and not the migrating Ni atoms. Thus, these point defects are the primary cause of the alloy restructuring, and their clustering and percolation to the surface dominate trends in the dynamics. Dislocation theory allows us to explore these atomic mechanisms, describing how these defects mediate surface segregation timescales and yielding a set of reactions responsible for surface-separating FCC alloy systems on the nanoscale [6].



**Figure 1.** In-situ HRTEM image of epitaxial  $\text{Cu}_2\text{O}$  and  $\text{NiO}$  grown on  $\text{CuNi}(100)$  alloy (10 at. % Ni) at  $350^\circ\text{C}$  and  $p\text{O}_2 = 0.1\text{ Pa}$  after 425 s



**Figure 2.** Surface energies for Cu surfaces with a single atomic Ni dopant in (a) the surface and (b) subsurface layers, respectively.

#### References

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