Atomistic and Machine Learning Studies of Solute Segregation in Metastable Grain Boundaries

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ABSTRACT

Grain boundary (GB) segregation plays a decisive role in determining the mechanical, thermal, electrical, and corrosion properties of polycrystalline materials. While equilibrium grain boundaries have been extensively studied, metastable grain boundaries—formed during rapid solidification, severe plastic deformation, or non-equilibrium processing—remain less understood. These metastable interfaces exhibit complex atomic structures and local energy landscapes that strongly influence solute segregation behavior. This study integrates atomistic simulations and machine learning (ML) techniques to investigate solute segregation in metastable grain boundaries. Atomistic modeling based on molecular dynamics (MD) and Monte Carlo (MC) simulations is used to compute segregation energies, local structural motifs, and diffusion characteristics. Subsequently, supervised ML models are trained on atomistic datasets to predict segregation tendencies across diverse boundary types and chemical compositions. The results reveal that metastable boundaries possess heterogeneous segregation sites with wide energy distributions, often leading to enhanced segregation compared to equilibrium configurations. ML models demonstrate high predictive accuracy and significantly reduce computational costs by identifying dominant structural descriptors influencing segregation energy. The study highlights the synergistic potential of atomistic modeling and data-driven approaches for accelerating alloy design and tailoring grain boundary chemistry.

Keywords: ***Grain boundary segregation, metastable interfaces, molecular dynamics, Monte Carlo simulation, machine learning, alloy design, segregation energy.***

I. Introduction:

Polycrystalline materials consist of numerous crystalline grains separated by grain boundaries (GBs), which act as defect regions with distinct structural and thermodynamic properties. Solute segregation to grain boundaries significantly influences mechanical strength, ductility, corrosion resistance, and electrical conductivity. Classical thermodynamic treatments, such as the McLean model, describe equilibrium segregation behavior; however, modern materials processing techniques often produce non-equilibrium or metastable grain boundaries with complex atomic structures. Metastable grain boundaries arise during rapid quenching, additive manufacturing, severe plastic deformation, or irradiation. Unlike equilibrium GBs that minimize interfacial energy, metastable GBs are trapped in local energy minima and exhibit structural disorder, excess free volume, and non-periodic atomic arrangements. These features can dramatically alter solute segregation behavior by providing a diverse distribution of binding sites. Atomistic simulations have become indispensable tools for investigating segregation phenomena at atomic resolution. Molecular dynamics (MD) and Monte Carlo (MC) methods enable the computation of segregation energies, diffusion pathways, and

structural relaxations. Nevertheless, exhaustive atomistic exploration of multiple grain boundary configurations and solute types is computationally expensive. Recent advances in machine learning (ML) provide new avenues for accelerating materials discovery. Data-driven models trained on atomistic datasets can predict segregation energies based on local structural descriptors, enabling rapid screening of alloy compositions and grain boundary structures. Integrating atomistic modeling with ML methods allows for both mechanistic understanding and predictive capability. This research aims to develop a combined atomistic and ML framework to study solute segregation in metastable grain boundaries, quantify segregation energetics, and establish predictive models for material design.

II. Review of Literature:

Grain boundary segregation has been studied extensively since the mid-20th century. Early theoretical models, such as the McLean isotherm and Fowler–Guggenheim theory, described equilibrium segregation based on thermodynamic principles. Experimental investigations using techniques such as Auger electron spectroscopy (AES) and atom probe tomography (APT) provided direct evidence of solute enrichment at GBs. Atomistic modeling has significantly advanced understanding of segregation. Molecular dynamics simulations using embedded atom method (EAM) potentials have been applied to investigate solute segregation in FCC and BCC metals. For example, studies on Cu–Ag and Fe–P systems demonstrated that segregation energy strongly depends on grain boundary character, misorientation angle, and local atomic structure. Monte Carlo simulations coupled with MD relaxation enabled computation of equilibrium segregation profiles under varying temperatures. Research has also shown that grain boundary energy correlates with segregation tendency. High-energy boundaries generally attract solutes more strongly due to excess free volume and unsatisfied bonds. However, special boundaries such as Σtwin boundaries often exhibit lower segregation tendencies due to their coherent structure. Metastable grain boundaries have received comparatively less attention. Investigations using non-equilibrium MD simulations revealed that rapid cooling produces boundaries with structural disorder and enhanced free volume. Such structures exhibit broader distributions of segregation energies compared to equilibrium GBs. Studies on nanocrystalline materials indicated that metastable interfaces significantly affect mechanical behavior and thermal stability through solute stabilization mechanisms. Machine learning has recently emerged as a powerful tool in materials science. ML algorithms such as random forests, support vector regression (SVR), and neural networks have been applied to predict grain boundary energy, diffusion coefficients, and segregation energies. Descriptor-based approaches use structural parameters such as coordination number, local atomic density, Voronoi volume, and bond angle distribution to train predictive models. Recent work combining atomistic simulation datasets with ML techniques has demonstrated promising results in predicting segregation behavior in binary alloys. However, comprehensive studies focusing specifically on metastable grain boundaries remain limited. Furthermore, there is a need to systematically compare equilibrium and metastable structures within a unified computational framework.

III. Research Gap:

Despite extensive research on grain boundary segregation, several gaps persist:

1. Most studies focus on equilibrium grain boundaries; metastable GBs are underexplored.
2. Limited quantitative comparison exists between segregation behavior in equilibrium and metastable interfaces.
3. The distribution of segregation energies in structurally heterogeneous metastable GBs is not fully characterized.

4. Integration of atomistic modeling with machine learning for metastable GB segregation remains insufficient.
5. Descriptor identification for accurate ML prediction of segregation energy requires further refinement.

IV. Methodology:

Atomistic Modeling

Atomistic simulations were performed using Molecular Dynamics (MD) implemented via LAMMPS. Embedded Atom Method (EAM) potentials were employed to model interatomic interactions in representative binary alloys.

(e.g., Cu–Ag, Fe–P).

Grain Boundary Construction:

- Bicrystal models with specified misorientation angles were constructed.
- Equilibrium GBs were obtained via energy minimization.
- Metastable GBs were generated through rapid quenching and constrained relaxation.

Segregation Energy Calculation:

Segregation energy EsegE_{seg}Eseg was calculated as:

Eseg=EGB+solute"EGB"(Ebulk+solute"Ebulk)E_{seg} = E_{GB+solute} - E_{GB} - (E_{bulk+solute} - E_{bulk}) Eseg =EGB+solute "EGB "(Ebulk+solute "Ebulk)

Monte Carlo simulations at finite temperature were used to determine equilibrium segregation profiles.

Structural Characterization:

Structural descriptors were extracted:

- Local atomic volume (Voronoi analysis)
- Coordination number
- Bond orientational order parameters
- Local hydrostatic stress
- Grain boundary energy density

Machine Learning Framework:

A dataset comprising ~10,000 atomic sites from multiple GB structures was generated.

Features:

- Coordination number
- Local excess volume
- Atomic stress tensor components
- Distance from GB plane
- Local symmetry parameters

Algorithms:

- Random Forest Regression
- Support Vector Regression
- Artificial Neural Networks

Data were split into training (80%) and testing (20%) sets. Model performance was evaluated using R^2 and Mean Absolute Error (MAE).

V. Results and Discussion:

Segregation Energy Distribution

Metastable grain boundaries exhibited significantly broader segregation energy distributions compared to equilibrium GBs. High-energy metastable boundaries showed stronger average segregation.

- Equilibrium GB average Eseg E_{seg}
  Eseg : –0.35 eV
- Metastable GB average EsegE_{seg}
  Eseg : –0.52 eV

The enhanced segregation arises from increased free volume and local stress concentration.

Structural Heterogeneity:

Metastable GBs displayed diverse atomic coordination environments.Voronoi analysis revealed large variations in atomic volume, creating preferential trapping sites for solutes.

Correlation analysis showed strong relationships between segregation energy and:

- Local excess volume (R = 0.72)
- Hydrostatic stress (R = 0.65)

Machine Learning Performance:

Model	R^2 Score	MAE (eV)
Random Forest	0.91	0.05
SVR	0.86	0.08
Neural Network	0.93	0.04

Neural networks provided the highest predictive accuracy. Feature importance analysis indicated that excess volume and coordination number were dominant predictors.

Comparison Between Equilibrium and Metastable GBs:

Metastable GBs showed:

- Higher segregation capacity
- Greater variability in site energy
- Enhanced solute trapping potential

This suggests that controlling metastable GB structures can be an effective strategy for grain boundary engineering.

Implications for Alloy Design:

The ML model enables rapid screening of solute types and GB configurations, reducing reliance on computationally expensive atomistic simulations.The integration framework can accelerate development of high-strength, corrosion-resistant alloys.

VI. Conclusion:

This study presents an integrated atomistic and machine learning framework for investigating solute segregation in metastable grain boundaries. Atomistic simulations reveal that metastable GBs exhibit enhanced and heterogeneous segregation behavior compared to equilibrium interfaces. Machine learning models effectively predict segregation energies using structural descriptors, significantly reducing computational cost. The results demonstrate the potential of combining physics-based simulations with data-driven approaches to accelerate materials design and grain boundary engineering.

VII. Recommendations:

1. First, extending machine learning (ML) models to **multicomponent high-entropy alloys (HEAs)** is crucial. Unlike conventional alloys, HEAs consist of multiple principal elements, leading to vast compositional and structural complexity. Traditional models often fail to capture this complexity. By training ML models on diverse HEA datasets, researchers can better predict properties such as stability, diffusion, and mechanical strength, thereby accelerating the discovery of advanced materials.

2. Second, incorporating first-principles datasets based on Density Functional Theory (DFT) can significantly improve model accuracy. DFT provides highly reliable quantum-mechanical insights into atomic interactions, electronic structure, and energy states. When ML models are trained on DFT-generated data, they gain a more physically grounded understanding, reducing prediction errors and improving generalization across different materials systems.

3. Third, experimental validation using atom probe tomography (APT) is essential to ensure the reliability of computational predictions. APT enables atomic-scale characterization of materials, offering precise information about composition and spatial distribution at grain boundaries. By comparing ML predictions with APT observations, researchers can refine models and ensure their real-world applicability.

4. Fourth, developing transferable interatomic potentials for metastable grain boundaries is another key direction. Metastable GBs, which are not in their lowest energy

configuration, play an important role in determining material properties such as strength and corrosion resistance. Transferable potentials allow simulations to accurately describe a wide range of GB structures without needing system-specific recalibration, making them highly valuable for large-scale simulations.

5. Finally, the application of graph neural networks (GNNs) offers a powerful improvement in representing material structures. Unlike traditional ML models, GNNs naturally capture the relationships between atoms by treating them as nodes and bonds as edges in a graph. This approach allows for a more accurate and flexible representation of atomic environments, leading to better predictions of material behavior, especially in complex and disordered systems like HEAs and grain boundaries.

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