

5. Theoretical and Computational Modelling studies on HEA Coatings

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Abstract

High-entropy alloys (HEAs) represent a class of materials with exceptional mechanical and tribological properties, making them ideal for advanced coating applications. This work presents a comprehensive exploration of HEA coatings using theoretical and computational models, incorporating molecular dynamics (MD) simulations, density functional theory (DFT), and dislocation analysis. Key findings demonstrate the superior performance of HEA coatings in improving wear resistance, reducing friction, and enhancing mechanical strength compared to pure metal substrates.

MD simulations reveal that HEA coatings, such as those comprising AlCoCrFeNi and FeCoNiTi, significantly mitigate crack propagation, lower dislocation density, and improve hardness by inducing atomic-scale distortions and solid-solution strengthening. Nanoindentation and wear tests further highlight reduced plastic deformation and wear volume loss in HEA-coated

materials. Furthermore, DFT calculations provide insights into the electronic interactions at interfaces, emphasizing the role of localized covalent bonding, charge redistribution, and orbital hybridization in reinforcing heterojunction stability and wear resistance.

Additionally, HEAs exhibit great potential for catalytic applications, with enhanced electron transport and active sites attributed to their multi-elemental configuration. Incorporating elements such as Mo improves catalytic performance through increased d-orbital contributions and reduced band gaps. This integrative approach combining MD and DFT modeling underscores HEA coatings' potential for applications in tribology, catalysis, and structural reinforcement.

Keywords: HEA coating simulations; molecular dynamics; density functional theory; structure-property correlations; mechanical behavior; wear resistance; catalysis

5.1 Introduction

5.1.1 High-Entropy Alloys

Throughout history, human civilization has consistently pursued the discovery and development of new materials, with metals and alloys playing a transformative role over millennia [1]. Right from the Bronze Age, alloy discovery has predominantly followed the “base element” paradigm, wherein a primary element, or occasionally two, constitutes the predominant concentration, with trace quantities of other elements [2]. Examples include iron in steels or nickel in superalloys. In contrast, a groundbreaking approach to alloy design emerged approximately a decade ago, advocating for the combination of multiple elements in near-equimolar proportions. Yeh et al. introduced high-entropy alloys (HEAs) that are multicomponent alloys consisting of five or more elements in near-equiatomic composition, crystallizing in simple solid solutions such as face centered cubic (FCC), body centered cubic (BCC), or hexagonal close packed structures [1].

The central concept of HEAs lies in maximizing the configurational entropy of mixing through equimolar composition, thereby stabilizing solid solution phases over competing phases, such as intermetallic compounds [3]. This novel design philosophy has significantly broadened the scope of alloy development, providing metallurgists with access to an expanded repertoire of materials with complex and tunable compositions.

5.1.2 High-Entropy Alloy Coatings

The diverse properties of HEA coatings can be attributed to the wide selection of constituent elements, encompassing carbide systems, transition metals, and refractory elements [4]. The ultimate performance of HEA coatings is influenced by their type, composition, and microstructure. HEA-based alloys and coatings have garnered significant attention in surface engineering applications due to their exceptional properties like high hardness, good oxidation resistance, corrosion resistance, high temperature stability, superior toughness [5] and potential utility in extreme environments. Recent years have witnessed rapid advancements in HEA coatings, with studies suggesting that traditional Ni-based superalloys, known for their high wear resistance, oxidation resistance, and hardness, could be replaced by HEA coatings incorporating nitrogen [6].

Broadly, HEA coatings can be categorized into three classes: (i) metallic HEA coatings, (ii) ceramic HEA coatings, and (iii) composite HEA coatings depending on the constituents. In the following sections, the two most important simulation methods for modeling HEA coatings are presented, namely, molecular dynamics (MD) [7] and density functional theory (DFT) simulations [8]. Various processing-structure-property relations that can be studied using these methods are presented in the following sections.

5.2 Molecular Dynamics simulations of HEA coatings

MD simulations play a pivotal role in elucidating the atomic-scale mechanisms that govern the properties and behavior of HEA coatings. A critical aspect of these simulations is the selection and application of interatomic potentials, which define the interactions between atoms within the system [9]. The derivative of the potential energy between atoms yields the interatomic forces at every point in time, which are then used to evolve the atoms in the simulation cell by means of updating the atomic positions and velocities using Newton's equations of motion. The following section outlines the principles and methodologies underlying the choice and implementation of interatomic potentials in MD simulations of HEA coatings.

Interatomic potentials, expressed through mathematical functions, describe atomic interactions within a material empirically. The accuracy of MD simulations is highly dependent on the chosen potential, as it directly influences the simulation's ability to replicate real-world phenomena, including mechanical properties, phase stability, and atomic bonding characteristics [10]. The common potentials used for simulations of HEA coatings are described below.

- a. **Embedded Atom Method (EAM):** The Embedded Atom Method is well-suited for modeling metallic systems, offering an efficient means to capture many-body interactions [11]. This potential has been extensively employed in simulations of HEAs due to its capability to represent the complex behavior arising from the diverse elemental compositions of these alloys.
- b. **Lennard-Jones Potential:** This potential is commonly utilized for modeling interactions between metal atoms and substrates or other phases present in HEA coatings [12] and is routinely employed for simulating non-bonded interactions.
- c. **Reactive Force Field (ReaxFF):** ReaxFF enables the modeling of dynamic processes, such as oxidation and phase transitions, by accounting for bond formation and breaking during simulations. Thus, ReaxFF is a valuable tool for exploring chemically reactive systems in HEAs [13].

5.2.1 Modeling the Deposition Process using Molecular Dynamics

MD simulations used to model HEA deposition processes are typically conducted within three-dimensional simulation cells. Periodic boundary conditions are applied along the horizontal x - and y -axes to simulate infinite planes, while a free boundary condition is maintained along the vertical z -axis to facilitate surface growth [14]. The deposition process involves sampling atom velocities from a Maxwell-Boltzmann distribution [15], with incident angles chosen randomly and a mean kinetic energy of 1 eV, reflecting the conditions of low-pressure argon magnetron sputtering [16]. This energy approximates the actual deposition environment, where the buffer gas randomizes the sputtered atom velocities without significant energy dissipation.

To ensure system stability during deposition, the positions of atoms in the bottom atomic layers are fixed. Simultaneously, a thermostat is applied to an intermediate zone to regulate temperature, maintaining isothermal conditions. The topmost layers of surface atoms are unconstrained, allowing them to respond dynamically to the incoming flux of atoms, thereby replicating the process of surface growth, as depicted in Fig. 5.1.

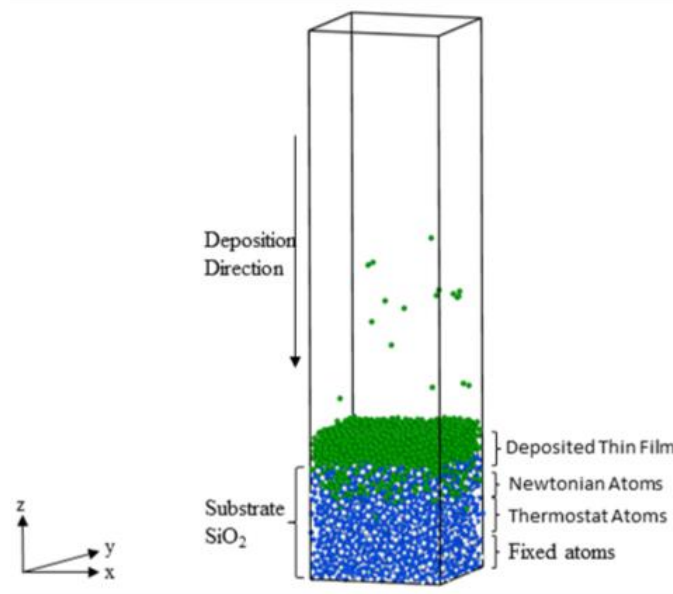


Figure 5.1: Atomistic snapshot of a simulation model depicting the deposition of HEA atoms during the formation of a HEA coating on a silica substrate using MD.

Alt Text: A simulation model displaying the thin film deposition of atoms by MD.

Though many MD software packages exist, the two most commonly used packages for thin film and coating simulations are the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [17] and the Groningen Machine for Chemical Simulations (GROMACS) [18] both of which are open source, supporting a wide variety of interatomic potentials and capabilities.

5.2.1.1 Controlling Deposition Parameters

The deposition parameters in thin film synthesis play a crucial role in tailoring the microstructure, crystallinity, and properties of HEA thin films. HEA films, composed of five or more principal elements in near-equiatomic proportions, exhibit unique mechanical, thermal, and chemical properties that are highly sensitive to deposition conditions [19, 20]. Key parameters such as substrate temperature, deposition rate, working pressure, and deposition angle significantly influence attributes like grain size, crystallographic orientation, surface roughness, and phase formation [21]. By optimizing these parameters through techniques like magnetron sputtering or pulsed laser deposition, it is possible to engineer HEA thin films with enhanced performance for applications in protective coatings, electronics, and energy systems [19, 21].

i. Substrate Temperature: Variations in substrate temperature significantly influence the microstructure of HEA coating films [19, 22]. For instance, in HEA thin films, increasing substrate temperature leads to enhanced adatom mobility and grain growth [23]. This results in a transition zone characterized by densely packed fibrous grains with smoother surfaces, as inter-grain voids diminish [24]. The elevated temperature promotes the formation of larger grains and can even lead to single-crystal growth, while lower temperatures favor the formation of polycrystalline films with smaller grains [25].

ii. Deposition Rate: The deposition rate significantly affects the surface morphology and grain structure of HEA thin films. Lower deposition rates during magnetron sputtering typically result in smoother surfaces with fine, spherical grains due to reduced adatom mobility and slower grain coalescence. In contrast, higher deposition rates lead to rougher surface morphologies and larger grain diameters, as the increased flux of deposited atoms promotes rapid grain growth and coalescence. This behavior is attributed to the balance between surface diffusion and atom arrival rates, which governs the microstructural evolution of HEA films during deposition [19, 25, 26].

iii. Deposition Temperature: In HEA thin films, elevated deposition temperatures enhance crystallinity and often promote preferred crystallographic orientations, such as along the (111) plane. For example, studies on HfNbTiVZr HEA thin films have shown that increasing the substrate temperature from room temperature to 275 °C transitions the microstructure from amorphous to a crystalline body-centered cubic (bcc) phase with strong $\langle 110 \rangle$ texture. Further increasing the deposition temperature to 450 °C leads to the formation of Laves phase precipitates within the bcc matrix, improving structural order and mechanical properties [27]. Similarly, TiZrNbTa-based HEA thin films deposited at higher temperatures exhibit enhanced crystallinity and phase stability due to increased adatom mobility, which facilitates atomic rearrangement into energetically favorable orientations. These findings highlight the critical role of deposition temperature in controlling the microstructure and crystallographic orientation of HEA thin films for advanced applications [28].

iv. Deposition Angle: The microstructure of HEA thin films varies significantly with the deposition angle during physical vapor deposition techniques such as magnetron sputtering. At small deposition angles (0° – 10°), dense and uniform microstructures are typically observed due to a more direct flux of atoms, which enhances surface coverage and reduces shadowing effects. In contrast, larger deposition angles (20° – 30°) lead to the formation of fine columnar grains growing perpendicularly to the substrate surface, as oblique angles increase shadowing and promote competitive grain growth. This angular dependence in microstructure evolution is critical for

tailoring the properties of HEA thin films, as it directly impacts their mechanical, thermal, and functional performance in advanced applications [19, 29, 30].

v. Substrate Orientation: The crystallographic orientation of the substrate significantly impacts atomic motion and density distribution in HEA thin films. For Fe substrates, high atomic density is concentrated along distinct planes such as (001), (011), and (111) [31]. These directions align with the close-packed directions of the respective substrates, where atomic interactions are strongest, interatomic distances are minimal, and migration energy requirements are lowest. In HEA thin films, this substrate orientation effect plays a crucial role in determining the film's microstructure and properties [19].

5.2.2 Mechanical Properties of HEA Coatings Using MD Simulations

As previously mentioned, molecular dynamics (MD) simulations serve as a powerful tool to investigate the atomic-scale mechanisms underlying the properties and behavior of HEA coatings. These simulations enable researchers to analyze phase stability, diffusion kinetics, and mechanical responses at the atomic level, offering insights that are often inaccessible through experimental techniques. By capturing the effects of temperature, composition, and strain on HEA coatings, MD simulations play a crucial role in predicting performance and optimizing material design for various applications.

i. Atomic-Level Mechanical Insights: MD simulations enable detailed exploration of the mechanical properties of HEA coatings, including wear resistance, hardness, and deformation mechanisms [32]. They can model processes such as phase transitions, dislocation activity, and lattice distortions, which significantly influence mechanical performance [33]. By simulating scenarios like high-pressure torsion or nanoscratching, these methods provide atomic-scale insights into how coatings respond to mechanical stress, revealing the underlying deformation mechanisms and aiding in the design of application-specific materials.

ii. Understanding Local Atomic Configurations: The inherently disordered atomic configurations in HEAs, resulting from high mixing entropy [34], can be comprehensively analyzed using MD. Such results are crucial for predicting the behavior of HEA coatings under varying conditions and optimizing their composition and structure for enhanced performance [35].

iii. Microstructural Evolution: MD simulations are instrumental in studying the microstructural evolution of HEA coatings during processes such as magnetron sputtering, thermal treatment, and thin-film deposition [36]. These simulations reveal how elemental composition affects the

morphology and atomic structure of coatings, providing valuable insights for tailoring properties to specific applications.

iv. Correlation with Experimental Data: By modelling atomic arrangements and comparing them with experimental results, such as X-ray diffraction patterns [37], MD simulations offer a robust validation framework. This correlation between simulation and experiment enhances the understanding of material properties and aids in refining theoretical models.

v. Modeling Environmental Interactions: MD simulations facilitate the study of interactions between HEA coatings and their environments, such as oxidation and corrosion processes [38]. These insights are critical for predicting the long-term reliability and durability of coatings in practical applications such as aerospace turbine blades, marine structures, biomedical implants, and industrial cutting tools [39].

vi. Thermal and Phase Behavior: The effects of heat on atomic behavior, including phase transitions and thermal stability, can be effectively modeled through MD. Temperature-controlled simulations mimic real-world conditions [40], such as those during sputtering or thermal cycling, providing a clearer understanding of material behavior under thermal loads.

vii. Dynamic Loading and Strain Rate Analysis: MD allows for the investigation of material behavior under dynamic loading conditions by simulating deformation mechanisms at various strain rates. This capability is vital for predicting responses to different loading scenarios [41].

viii. Long-Term Processes and High-Throughput Screening: Advanced methodologies in MD extend the ability to study [42] as diffusion and phase transformations, even within the constraints of computational resources. In the molecular dynamics (MD) simulations, the term ‘long-term’ typically refers to time scales that extend beyond the nanosecond range, reaching into microseconds or even milliseconds, while traditional MD simulations are often limited to shorter time scales of nano and picosecond due to computational constraints. Additionally, MD facilitates high-throughput screening of material compositions and configurations [43], accelerating the discovery of novel HEA coatings with tailored properties.

MD simulations provide valuable insights into the mechanical and tribological properties of HEA coatings, which are applied to substrates such as aluminum (Al) [44] nickel (Ni) [45] titanium (Ti) [46], and copper (Cu) [47] to enhance their performance in diverse industrial applications. These coatings address the limitations of bare substrates, such as low hardness, poor wear resistance, and susceptibility to oxidation, by significantly improving mechanical strength

and durability. Yang et al. [44] used MD simulations package, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to reveal that AlCoCrFe HEA-coated Al exhibits significantly improved mechanical properties such as Young's modulus, hardness and wear resistance compared to pure Al (see Fig. 5.2 (a)).

Figure 5.2(a) visualizes the deformation of both pure aluminum and the HEA-coated aluminum during nanoindentation, using OVITO [48]. The figure displays the atomic deformations at both the maximum indentation depth and after the indenter is retracted. Atoms affected by the indenter's pressure exhibit increased potential energy, indicated by color in the figure. For pure aluminum, the first row of Figure 5.2(a) shows the deformation at maximum indentation depth, while the second row shows the deformation after retraction. Beyond the indentation itself, some surface atoms are also deformed, having been extruded outwards. Upon retraction, the indentation's projected area shrinks due to elastic recovery.

In contrast, the third and fourth rows of Figure 5.2(a) depict the deformation of the HEA-coated aluminum at maximum indentation depth and after retraction, respectively. The indentation mark diameter for pure aluminum reaches approximately 68 Å, whereas it's only about 25 Å for the HEA-coated aluminum, demonstrating the coating's greater hardness. Furthermore, the HEA-coated aluminum's surface remains significantly smoother during indentation, with fewer protruding atoms compared to pure aluminum. This smoothness persists after retraction. These differences in behavior stem from the HEA layer's higher Young's modulus and hardness.

In another study, Li et al. [47] showed that reduced dislocation nucleation, by virtue of the locking of Hirth dislocations in a FeNiCrCoCu HEA coating on Cu, was very effective in reducing subsurface damage. To investigate how an HEA coating affects the wear of a copper substrate, the number of displaced copper atoms was measured. In molecular dynamics simulations, the number of displaced atoms is often used as a proxy for wear volume, as atomic volume is difficult to calculate. Here, a "wear atom" is defined as a copper atom in an amorphous region that has moved more than 3.615 Å [49] (the copper lattice constant) from its original position. Common Neighbor Analysis (CNA) [50] was used to identify the crystal structure types. As shown in Fig. 5.2 (b), Cu-based HEA coatings exhibited fewer wear atoms, defined as atoms displaced beyond the lattice constant, compared to pure Cu [47]. Less wear volume indicates that the coating significantly reduces material loss and enhances durability. Mishra et al. [51] studied MoWCoTaZr HEA coating on Ni using MD simulations (see Fig. 5.2 (c)) and showed that during indentation, various dislocation types including Shockley partials, stair-rod partials, and Hirth partials, were observed in the Ni-based HEA coatings. These dislocations, along with prismatic and V-shaped loops, indicate active crystal slip planes, contributing to high stiffness and hardness in the coated material.

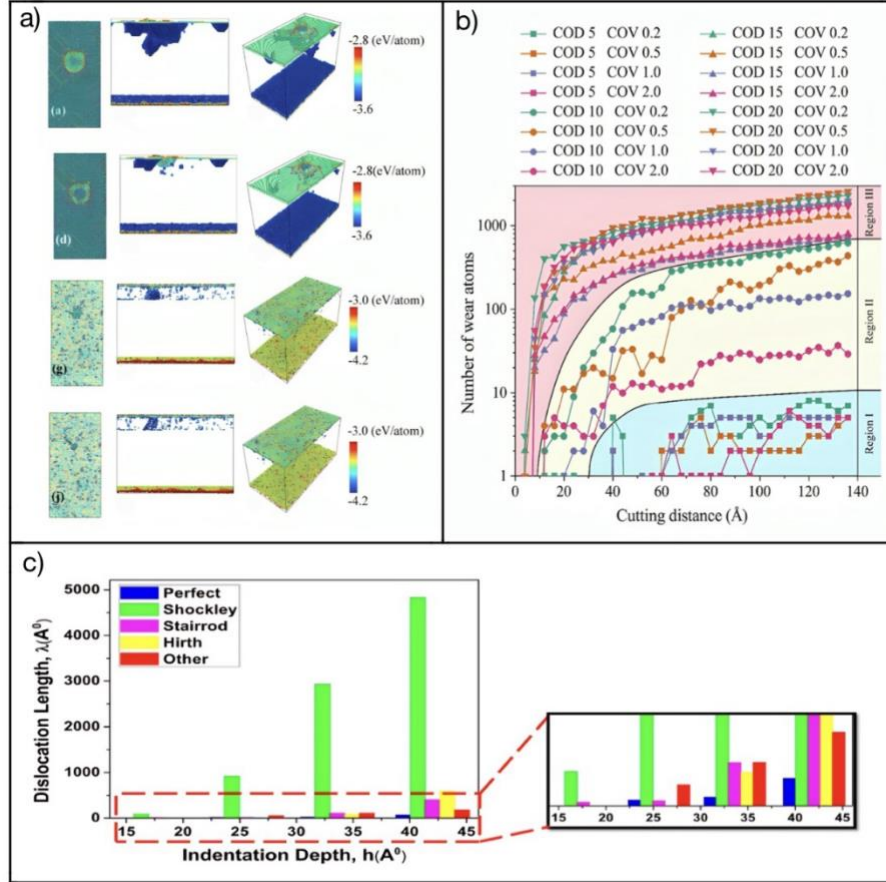


Figure 5.2: Effect of indentation depth on the strain, dislocation length (a) Simulated deformations at either the maximum nanoindentation depth or after the indenter retraction [44], (b) The number of wear atoms in the HEA coated Cu substrate [47], (c) The evolution of different types of dislocations for single crystal Ni – HEA specimen along with enlarged view [51]. *Reproduced (a) with permission from [44] © 2021 Elsevier B.V, (b) from [47] © 2021 Elsevier B.V and (c) from [51] © 2019 Taylor and Francis.*

Alt Text: (a) Snapshots of the nanoindentation process and (b and c) characterization of wear atoms and dislocation types during wear and indentation.

Indentation simulation is a powerful tool for understanding and predicting the mechanical behavior of materials under indentation. It involves creating a model of the indentation process and using numerical methods to simulate the deformation of the material. Nanoindentation is a powerful technique used to study the mechanical properties of materials at very small scales. During nanoindentation, HEA-coated Al exhibits lower plastic deformation and greater recovery due to elastic deformation compared to pure Al. The calculated Young's modulus of this material is 119.30 GPa, which is much higher than that of pure Al (79.93 GPa). Similarly, hardness increases from 7.25 GPa for pure Al to 79.58 GPa for the coated sample. Post-indentation, the reduced projected (calculated using Sneddon's equation) area and smoother surface near the indentation confirm the superior hardness and elastic recovery of HEA-coated Al [44].

In another study, Li et al. [47] showed that reduced dislocation nucleation, by virtue of the locking of Hirth dislocations in a FeNiCrCoCu HEA coating on Cu, was very effective in reducing subsurface damage. To investigate how an HEA coating affects the wear of a copper substrate, the number of displaced copper atoms was measured. In molecular dynamics simulations, the number of displaced atoms is often used as a proxy for wear volume, as atomic volume is difficult to calculate. Here, a "wear atom" is defined as a copper atom in an amorphous region that has moved more than 3.615 Å [52] (the copper lattice constant) from its original position. Common Neighbor Analysis (CNA) was used to identify the crystal structure types. Less wear volume indicates that the coating significantly reduces material loss and enhances durability. Mishra et al. studied MoWCoTaZr [51] HEA coating on Ni using MD simulations (see Fig. 5.2 (c)) and showed that during indentation, various dislocation types including Shockley partials, stair-rod partials, and Hirth partials, were observed in the Ni-based HEA coatings. These dislocations, along with prismatic and V-shaped loops, indicate active crystal slip planes, contributing to high stiffness and hardness in the coated material.

High-entropy alloy (HEA) coatings exhibit exceptional mechanical properties, making them promising candidates for improving wear resistance and durability on various metal substrates. To better understand their behavior under different mechanical conditions, atomistic simulations are employed to analyze indentation and cutting processes. Figure 5.3 presents atomistic snapshots of HEA coatings on various metal substrates, illustrating different mechanical simulations. Fig 5.3 (a) illustrates a HEA coating on a Cu substrate is subjected to indentation using a spherical indenter with a 4 nm radius to analyze the mechanical properties of the coated material [53]. Fig 5.3 (b) depicts the nano-scratching of an AlCoCrFeNi HEA coating on a Ni substrate simulated using a model that incorporates both the workpiece and the cutting tool [45]. Fig 5.3 (c) shows HEA coating on a Cu substrate undergoes a two-step wear performance evaluation: first, an abrasive particle indents the model at a speed of 0.1 Å/ps until it reaches the

target cutting depth (COD), followed by cutting along the negative x-axis at a predetermined cutting velocity (COV) [47]. A HEA coating on a Ti substrate is analyzed under similar conditions, where indentation occurs at a speed of 1 Å/ps before wear performance is assessed through cutting along the negative y-axis at a specified COV [46].

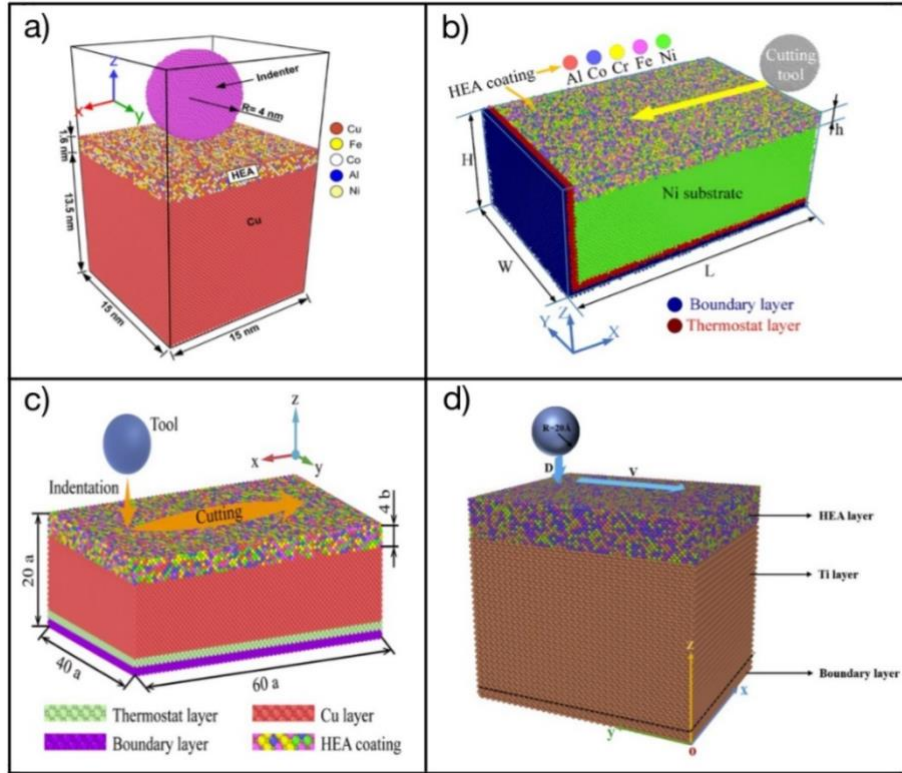


Figure 5.3: Atomistic snapshots of HEA coatings on various metal substrates: (a) Atomistic snapshots of HEA coatings on various metal substrates: (a) HEA coating on a Cu substrate under indentation with a 4 nm spherical indenter [53], (b) Nano-scratching of an AlCoCrFeNi HEA coating on a Ni substrate using a cutting tool [45], (c) HEA coating on a Cu substrate undergoing indentation and cutting to evaluate wear performance [47], (d) HEA coating on a Ti substrate subjected to indentation and cutting along the negative y-axis [46]. *Reproduced (a) with permission from [53] © 2019, The Indian Institute of Metals – IIM, (b) from [45] © 2022 The Society of Manufacturing Engineers. Published by Elsevier Ltd, (c) from [47] © 2021 Elsevier B.V, (d) from [46] © 2023 Elsevier Ltd.*

Alt Text: Atomistic snapshots of HEA coatings on various metal substrates.

5.2.2.1 Friction and Wear resistance of HEA coatings

Several studies have focused on the frictional properties and wear resistance of HEA coatings. For instance, Ren et al. [46] studied the effect of FeCoNiTi coating on Titanium (Ti) and observed that the HEA-coated Ti demonstrates higher frictional forces (inversely proportional to coefficient of friction) and improved wear resistance compared to pure Ti. The coefficient of friction for pure Ti and HEA-coated are 1.3 and 0.6 respectively [46]; furthermore, it was observed that the coefficient of friction (COF) for HEA-coated Ti decreased with respect to cutting velocity due to strain rate hardening and thermal softening, which highlighted the enhanced wear resistance of the coating. Conversely, an increased cutting depth led to an increase in the frictional forces across all models (including HEA coatings), which was attributed to the larger surface interaction areas. In the same study, the wear resistance of FeCoNiTi HEA coating on Ti is also discussed. Scratching induced fewer dislocations in the HEA coating compared to pure Ti. This difference likely stems from two factors. First, the thinness of the coating makes dislocation nucleation in the FCC and BCC structures more difficult. Second, the HEA coating exhibits a higher stacking fault energy after relaxation. The presence of the HCP phase in the relaxed FeCoNiTi HEA coating contributes to its higher stacking fault energy. This HCP phase effectively stabilizes the coating. Since dislocation probability is inversely related to stacking fault energy, this higher energy makes dislocation formation less likely. Consequently, increasing stacking fault energy correlates with a decrease in overall dislocation density, including both dislocations within the cell and at cell walls. This, in turn, leads to a reduction in stress. They showed that HEA coatings reduce the dislocation density in Ti, preventing the propagation of dislocations and minimizing plastic deformation.

In another study, Li et al. [47] simulated the frictional properties in a FeNiCrCoCu coating on copper and found that for Cu-based HEA coatings, a linear relationship was observed between the cutting depth and tangential force from the abrasive particle (indenter). Moreover, the friction coefficient increased with cutting depth but decreased with cutting velocity, which was driven by thermal softening and strain rate effects. It was also found that the HEA coatings reduced substrate damage and minimized internal defects by decreasing the number of wear atoms, even at higher velocities. Doan et al. [45] studied the performance of AlCoCrFeNi HEA coating and demonstrated that Ni-based HEA coatings show large frictional force compared to pure Ni, indicating greater wear resistance and toughness (refer to Fig. 5.4(a)). The COF for HEA-coated Ni was higher (0.83) than that of pure Ni (0.73), demonstrating the superior adhesion, toughness, and strength of the HEA coating.

MD simulations also offer critical insights into the stress-strain behavior, dislocation dynamics, and wear resistance of HEA coatings. These coatings, when applied to substrates including aluminum (Al), titanium (Ti), copper (Cu), and nickel (Ni), significantly enhance mechanical and tribological properties by improving hardness, reducing wear, and minimizing dislocations. Yang et al. [44] studied the stress-strain behavior of AlCoCrFe HEA coating on Aluminum (Al) substrate. As shown Fig. 5.4(b), shear strain accumulates around the indenter tip as deformation occurs under the applied load (P), perpendicular to the coated interface. The color bands indicate that shear strain intensity, and consequently deformation, increases with indentation depth. This deformation is concentrated near the indenter tip due to greater plastic strain accumulation in that region. Increased pile-up on the hard, incoherent HEA interface layer leads to a more dispersed shear strain distribution. Yang et al. [44] they observed that pure Al develops cracks during nanoindentation, whereas HEA-coated Al does not. This result indicates that HEA coatings suppress crack formation, resulting in lower maximum strain and higher maximum stress in the coated material. Besides, tribological performance was significantly enhanced with HEA coatings, as evidenced by the reduced depth and width of wear tracks and smaller wear volume losses compared to pure Al. The HEA coating significantly reduces the total dislocation length in aluminum. While pure aluminum exhibits a total dislocation length of 3073.79 Å, the HEA-coated aluminum shows a dramatically lower value of only 66.76 Å. Therefore, the dislocation density was lower in the HEA-coated Al, suggesting reduced plastic deformation and superior wear resistance. The COF for HEA-coated Al was observed to be much lower (0.14) than that of pure Al (0.62), demonstrating the coating's ability to minimize wear and enhance durability [44].

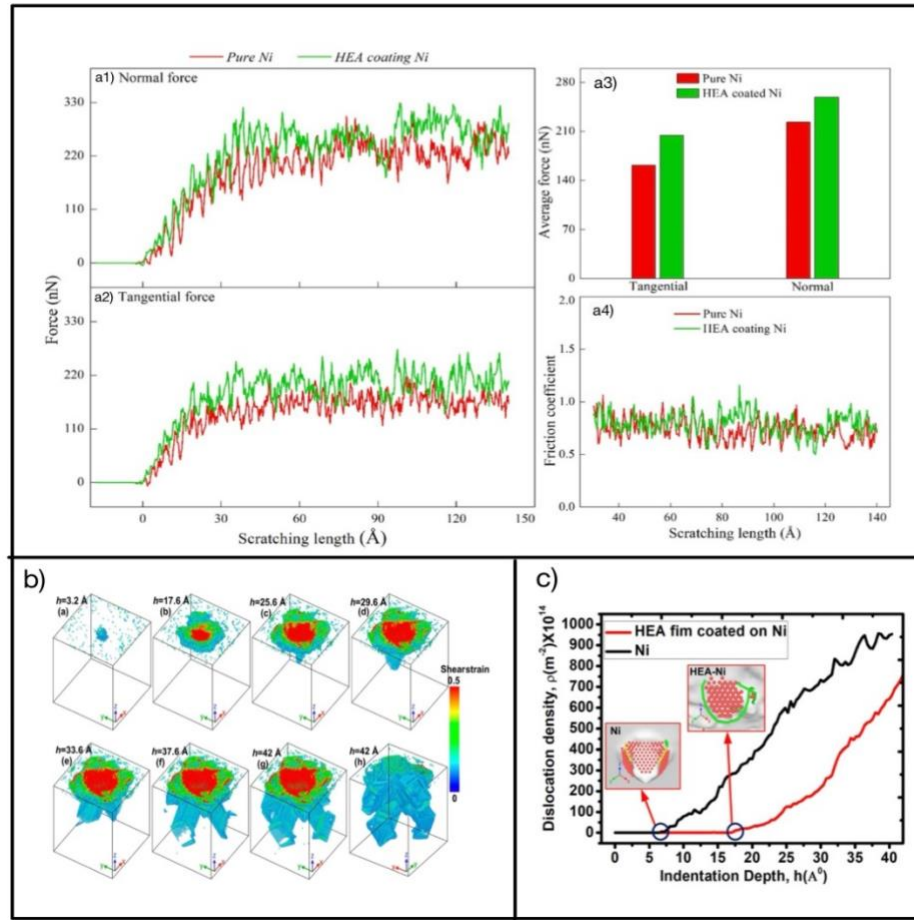


Figure 5.4: (a) Comparison of force components (a1–a2), average force (a3), and friction coefficient (a4) during the scratching processes of pure Ni substrate and AlCoCrFeNi HEA coating on Ni substrate at a cutting depth of 15 Å and a scratching velocity of 50 m/s [45], (b) Atomic snapshots of shear strain for different indentation depth from (a) $h = 3.2$ Å to (g) $h = 42$ Å from top view and (h) $h = 42$ Å from side view for Single Crystal Ni – HEA specimen [45] (c) Plot of dislocation density versus indentation depth (ρ – h) curves for both Single Crystal Ni – HEA and Single Crystal Ni specimen [51]. *Reproduced (a) with permission from [45] © 2022 The Society of Manufacturing Engineers. Published by Elsevier Ltd, (b) and (c) from [51] © 2019 Taylor and Francis.*

Alt Text: (a) force distribution during scratching simulation in Ni-HEA coating; (b) shear strain distribution in a Ni-HEA sample with respect to indentation depth and (c) variation of dislocation density with indentation depth.

In another study by Mishra et al. [51], **Figure 5.4(c)** illustrates the variation in dislocation density (ρ) as a function of indentation depth (h) for HEA-SC Ni and SC Ni. Dislocation density is calculated as the total dislocation length (λ) per unit volume (V). In SC Ni, dislocations begin to nucleate around $h \sim 6 \text{ \AA}$, while HEA-SC Ni exhibits a delayed onset of dislocation nucleation at approximately $h \sim 17.2 \text{ \AA}$. Beyond these initial nucleation points, increasing stress at the interface activates multiple slip systems, leading to the generation of more dislocations and increased interaction probability. This results in a sharp rise in dislocation density with increasing indentation depth. Generally, aside from some minor fluctuations, dislocation density increases with indentation depth after the initial nucleation and reaches a maximum as Shockley partial nucleation progresses. The HEA coating significantly improves wear resistance through mechanisms such as solid solution strengthening, atomic size differences, and increased stacking fault energy. These mechanisms work together to reduce flow stress and dislocation density, ultimately leading to a more durable and wear-resistant surface. An observed FCC-to-BCC phase transition during relaxation enhances wear resistance through an increase in hardness and reducing ductility.

5.3 Density Functional Theory (DFT) simulations of HEA coatings

The DFT method has been particularly well-suited for modeling complex systems such as HEAs. DFT solves the quantum mechanical problem of interacting electrons in a material [53]. Rather than directly dealing with the complexity of each electron's wave function, DFT simplifies this many-body problem by using the electron density as the fundamental variable. This approach allows for a tractable solution to the Schrödinger equation [53], enabling the accurate prediction of material properties based on the distribution of electrons in the system.

For HEA coatings, DFT is particularly valuable in understanding the underlying electronic interactions that govern their unique behavior. By modeling key electronic properties such as the band structure and the density of states (DOS), Density Functional Theory (DFT) enables the prediction of structural, mechanical, electronic and thermal properties of HEAs [54]. DFT provides insight into how electrons are distributed and how they contribute to the material's overall performance. The ability of Density Functional Theory (DFT) to model electronic properties is crucial for predicting the effects of alloying elements [55], understanding atomic-level mechanisms of wear [56] and corrosion resistance [57, 58] and evaluating the stability of phases within an alloy.

Additionally, DFT simulations offer a means to explore, charge density distributions [59] and the partial density of states (PDOS) at interfaces [59] between HEA coatings and other materials. These properties are integral to optimizing HEA coatings for specific applications, including tribological performance and catalytic behavior. In sum, DFT offers a comprehensive toolset for probing the atomic and electronic interactions within HEAs, thereby advancing the understanding of their complex material properties. Popular DFT simulation packages include the Vienna Ab initio Simulation Package (VASP), a commercial package [59] that employs the plane-wave basis sets and the projector augmented-wave (PAW) approach to address core-electron interactions [59] and Quantum ESPRESSO, an open-source software for calculating electronic structures with plane-wave basis sets and pseudopotentials [60].

5.3.1 DFT Modelling Parameters

In any DFT-based investigation of HEA coatings, several critical parameters must be carefully defined to ensure both accuracy and computational efficiency. These include:

- i. **Exchange-Correlation Functionals:** One of the central approximations in DFT is the treatment of electron-electron interactions [59]. This is handled by the exchange-correlation functional, which accounts for the exchange and correlation energies between electrons. The Generalized Gradient Approximation (GGA) [59], and specifically the Perdew-Burke-Ernzerhof (PBE) functional [53], is widely used due to its balance between accuracy and computational cost.
- ii. **k-Points Grid:** In DFT, the electronic properties of the material are sampled over a set of points in the Brillouin zone, referred to as k-points [61]. The density of the k-points grid determines the resolution of the electronic wavefunctions and, consequently, the precision of calculated properties such as the total energy and the electronic structure. A finer k-points grid leads to more accurate results but requires more computational resources.
- iii. **Energy cutoffs:** DFT employs a plane-wave basis set to describe the electronic states within the material [62]. The energy cutoff defines the maximum kinetic energy of the plane waves included in the simulation. Higher energy cutoffs generally yield more accurate results, but they also increase the computational expense. Therefore, selecting an appropriate cutoff energy is critical for achieving a balance between precision and computational efficiency.

- iv. **Convergence Criteria:** To ensure that the simulation has reached a stable and optimized solution, convergence criteria are applied. These criteria dictate the acceptable limits for changes in total energy, forces on atoms, and atomic displacements during the relaxation process [63]. The relaxation process in Density Functional Theory (DFT) simulation refers to the process of minimizing the system's energy by adjusting atomic positions until a stable configuration is reached. This process is essential to ensure that the system is in a low-energy equilibrium state, which accurately represents the material's actual structure. Careful setting of these parameters ensures that the calculated properties accurately reflect the material's true behavior.

The accuracy of DFT simulations for HEA coatings eventually depends significantly on the choice of computational parameters. Below, two representative studies demonstrate the application of DFT parameters in modeling HEA coatings and analyzing their properties.

5.3.2 Basic Terminologies and Concepts

Before delving into the applications of DFT simulations in modeling HEA coatings, it is important to understand some key concepts such as band structure, DOS, and PDOS. These concepts are fundamental to connecting the electronic properties of materials with their mechanical, chemical, and tribological behavior, as described below.

5.3.2.1 Band Structure:

The band structure of a material is a graphical representation of the allowed energy levels (bands) for electrons as a function of their momentum. It tells us how electrons behave in different regions of a material, which directly influences its conductivity, elasticity, and other properties [64]. In materials, these energy bands are typically classified into the valence band (filled with electrons) and the conduction band (unfilled or partially filled with electrons). The energy gap between these bands, known as the bandgap, plays a critical role in determining whether a material behaves as a conductor, semiconductor, or insulator. Metals have overlapping conduction and valence bands, meaning there is no bandgap, allowing electrons to move freely and conduct electricity. Semiconductors have a small bandgap that electrons can jump across under certain conditions (e.g., heat or light), while insulators have a large bandgap, preventing electron movement under normal conditions [65].

5.3.2.2 Density of States (DOS):

While the band structure provides detailed information about the energy-momentum relationship for electrons, the DOS focuses on the number of electronic states available at each energy level within a material [66]. Furthermore, since DOS is a function that represents how many electron states exist at each energy level, it provides a way to quantify how many electron states are present at different energies in a solid. In a conductor, the DOS at the Fermi level (the highest occupied energy level at absolute zero) [67] is particularly important because it indicates the number of states available for conduction.

The shape of the DOS curve can tell us a lot about the electronic behavior of a material. A high DOS near the Fermi level indicates many available electronic states, which can lead to better conductivity. In contrast, a low DOS at the Fermi level suggests fewer states are available for electron movement, as in the case of semiconductors or insulators [65]. A related quantity, the PDOS goes one step further by breaking down the total DOS into contributions from specific atoms or orbitals within the material [68]. Such an analysis is particularly useful for materials like HEAs, where multiple elements contribute to the electronic structure. PDOS helps to identify how individual elements or specific orbitals (such as *s*, *p*, *d*, or *f* orbitals) contribute to the overall electronic behavior. For example, in an HEA composed of multiple metallic elements, the PDOS can show how each element's d-orbitals contribute to the bonding and electronic properties of the material [69]. In the following sections, various applications of DFT simulations on HEA coatings involving phenomena such as mechanical properties, tribological properties and catalysis are elucidated.

5.3.3 Applications of DFT simulations in HEA coatings

5.3.3.1 Mechanical Properties and Reinforcement effect in HEA Coatings

Li et al. [71] studied the strengthening mechanisms and elastic properties of AlCoCrFeNiMo_{0.8} – TiC HEA composite coatings using DFT simulations performed with the CASTEP package [72] the GGA-PBE functional [53]. Their results demonstrated the durability of the HEA coatings for high strength applications arising from enhanced phase stability and strengthening mechanisms. The authors created Special Quasi random structure (SQS) supercells [72] (see Fig. 5.5(a) for the B2 and σ phases and examined their elastic characteristics, calculating the shear and Young's moduli for each phase. In the AlCoCrFeNiMo_{0.8}-TiC composite coating, precipitation strengthening was determined to be the primary mechanism responsible for enhancing the material strength and hardness. A newly designed, highly accurate, hardness prediction model was proposed by the authors, which had a relative error of only 9.1% when compared to experimental nanoindentation data.

In a study by Liang et al. [73], the charge density distribution between different atoms at the TiN/CoTi interface was studied. As shown in Fig. 5.5(a), the localized electron interactions, particularly between N and Co atoms are visualized. The shared electron cloud between these atoms indicates a strong N-Co covalent bond near the interface, which plays a key role in improving the bonding strength of the heterojunction. The strong polar covalent bonds between Co and N atoms enhance the interface bonding, crucial for the stability of the HEA coating. This localized bonding behavior was found to be essential for reinforcing the mechanical integrity of the TiN phase in the coating, contributing to its wear resistance and durability. Further analysis shows significant charge transfer around the Co and Ti atoms (Fig. 5.5 (b)), with electrons depleting from Co atoms and accumulating around N atoms. The formation of N-Ti covalent bonds in TiN remains a dominant force, and the strong N-Co bonds at the interface provide additional stability. This finding reinforces the idea that covalent bonding between N and Ti is stronger than metallic bonds, making TiN a robust reinforcing phase within the HEA. Additionally, as shown in Fig. 5.5(c), the PDOS plot gives further insights into the electronic interactions contributing to the stability and reinforcing effect of the TiN phase. The PDOS at the interface showed that the heterojunction has a strong metallic character, particularly due to the hybridization between Co-3d and N-2p orbitals. The N-Co bond contributes significantly to the wear resistance of the HEA coating as this bond stabilizes the interface and enhances the ability of the material to withstand stress and wear. The dominance of Co-3d and N-2p orbital interactions in the bonding region suggests that the electronic coupling at the interface strengthens the shear-resistant nature of the coating. This enhances the reinforcing effect of TiN in the HEA by providing mechanical stability and wear resistance. Additionally, the comparison of the PDOS contributions from Ti, N, and Co atoms showed that the hybridization of orbitals from these atoms plays a critical role in defining the mechanical behavior of the HEA coating [73].

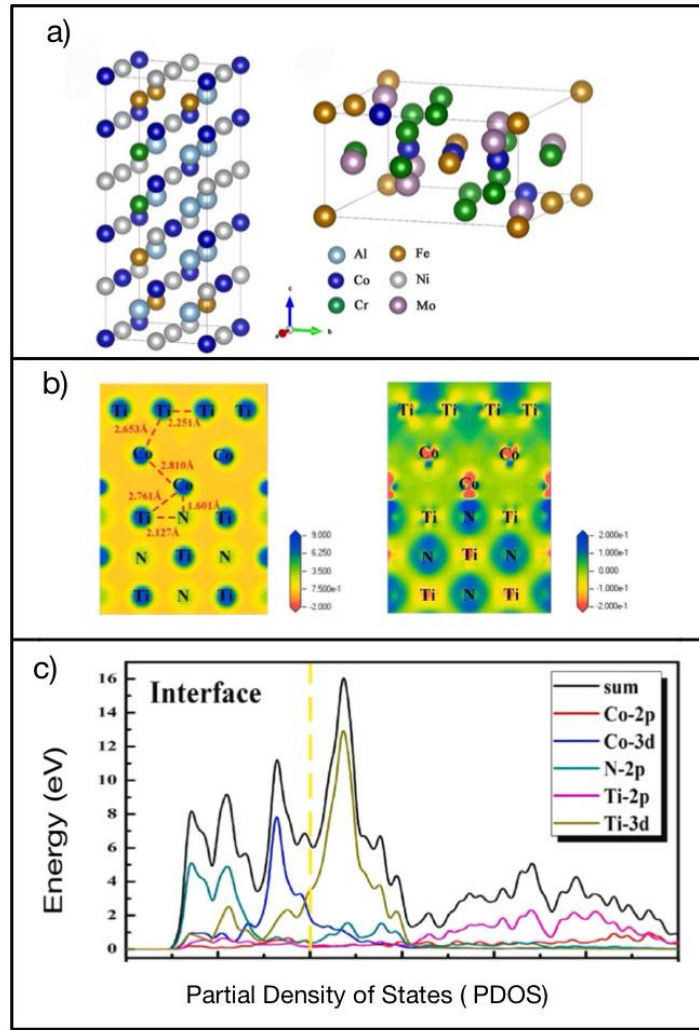


Figure 5.5: (a) The B2 phase of HEA Coating with Al, Fe, Co, Ni, Cr, and Mo atoms [72]. (b) Charge density and charge density difference of heterojunction [73], (c) PDOS for the interface zone of TiN/CoTi₂ heterojunction [73]. *Reproduced (a) from [70] © 2023, the author(s), under exclusive license to Springer Science Business Media. (b, c) with permission from [73] © 2022 Elsevier.*

Alt Text: (a) atomistic snapshot of B2 phase in AlFeCoNiCrMo HEA (b) charge density difference plots (c) Partial density of states (PDOS) from DFT simulations of HEA coatings.

5.3.3.2 Tribological Properties and Wear Mechanism

Lu et al. [74] used DFT simulations with the CASTEP simulation package to study the structural evolution and tribological properties of FeCoNiCrMo HEA coatings processed through laser remelting and tempering. Using the GGA-PBE functional [53], they modeled the structural and electronic properties of the coatings providing crucial insights into the nanoscale tribological behavior of these coatings (see Fig. 5.6 (a)). Emphasizing the interplay between their structural features and performance, the study revealed that the FeCoNiCrMo HEA coatings undergo a transformation in preferred crystal growth direction from (200) to (220) due to laser remelting (LR) and tempering (TP), with TP promoting isotropic phase formation. The coatings displayed varying tribological performance, with TP-HEA exhibiting the lowest wear rate and smoothest COF curve, while LR-HEA showed the highest wear rate. DFT calculations were also performed to characterize the differential charge density, which evaluates the distribution of charge between atoms at the interface of the Si_3N_4 tribo-pair and the HEA surfaces. As seen in Figs. 5.6 (b) and (c), the blue regions represent areas of high charge density where electrons accumulate, indicating stronger interactions whereas the red regions indicate low charge density where weaker interactions or charge depletion occurs. Such a charge distribution calculation helps to identify the strength of interatomic forces between the HEA atoms and the Si_3N_4 tribo-pair, which is critical in understanding the wear process. The weak forces between these atoms, as indicated by the analysis, suggest a low wear resistance at specific sites. In addition to the above, DFT allows calculation of the average potential energy of various crystal planes. The authors report an average potential energy of 4.036 eV for the (200) plane, 3.787 eV for the (220) plane and 3.970 eV for the (111) plane. These values represent the potential energy landscape experienced by atoms at the surface during wear. The higher potential values observed at the atomic boundaries (between adjacent atoms) suggest that these regions are more energetically stable, which may correlate with lower wear in those areas. The higher charge densities at the boundaries and larger average potentials (as calculated for the (200) and (111) planes) suggest stronger interatomic forces, which would increase the COF of the HEA coatings. [56]

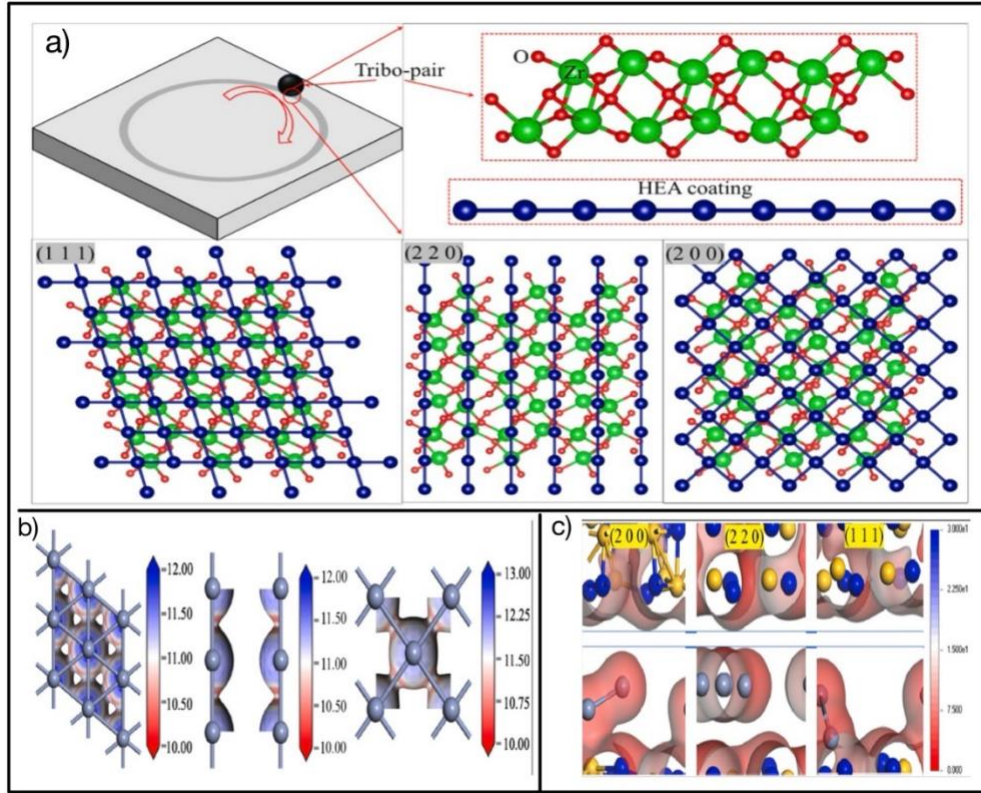


Figure 5.6: (a) Schematic illustration of the tribological pair and the cleaved crystal planes of the HEA coating [56] (b) differential charge density of (111), (220) and (200) crystal planes [56], (c) differential charge density distribution of wear model [56]. *Reproduced (a,b,c) with permission from [56] © 2024 Elsevier Ltd.*

Alt Text: (a) Tribo-pair and cleaved planes in a HEA coating (b) and (c) Differential Charge density and charge density distribution plots from DFT simulations of HEA coatings.

5.3.3.3 HEA Coatings as catalysts

Huo et al. [74] performed DFT simulations of CoCrFeNiAl and CoCrFeNiMo HEA coatings with the aim of better understanding their catalytic efficiency. The synergistic effect in HEAs results from complex interactions between the principal elements, which impact their electronic structure, charge distribution, and overall catalytic efficiency. The random distribution of components in CoCrFeNiAl and CoCrFeNiMo causes localized fluctuations in electronic states, influencing electron mobility and charge transfer. Furthermore, the natural porous nature of HEAs,

resulting from their multi-element composition, expands the surface area available for electrochemical processes. This increased surface area is critical for catalytic reactions like water splitting, since active sites contribute to the adsorption and dissociation of water molecules.

Figures 5.7 (a) and (b) show Projected Density of States (PDOS) plots, providing insights about the electronic states that are accessible for catalytic activity. CoCrFeNiMo has a larger PDOS around the Fermi level than CoCrFeNiAl, indicating a greater availability of electronic states that facilitate charge transfer. This shows that the inclusion of Mo adds new states, enhancing catalytic performance by allowing efficient electron transport inside the porous HEA structure and accelerating reaction kinetics. The CoCrFeNiMo alloy (Fig. 5.7 d) has a lower energy band gap than CoCrFeNiAl (Fig. 5.7 c), implying that CoCrFeNiMo allows for quicker electron transport, which is essential for catalytic events. A smaller band gap reduces charge transfer resistance and enhances electron mobility, improving the efficiency of electrochemical reactions. Thus, the results demonstrate that CoCrFeNiMo's enhanced surface area, electronic structural changes, and synergistic interactions all contribute to its higher catalytic efficiency when compared to CoCrFeNiAl.

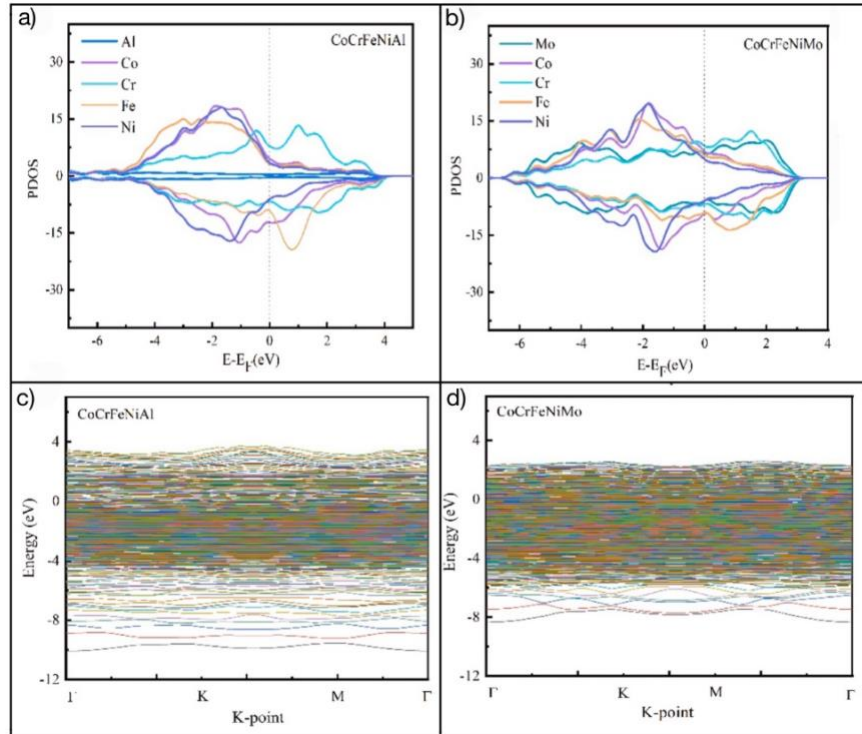


Figure 5.7: (a) PDOS of CoCrFeNiAl HEA, (b) PDOS of CoCrFeNiMo HEA, (c) energy bands of CoCrFeNiAl HEA, and (d) Energy bands of CoCrFeNiMo HEA [74]. *Reproduced with permission from [74] © 2024 Elsevier B.V.*

Alt Text: Partial Density of States and energy bands in HEA systems.

5.4 Conclusions and Outlook

This chapter has provided an in-depth exploration of theoretical and computational modeling approaches for HEA coatings, emphasizing their exceptional potential to improve wear resistance, mechanical performance, and catalytic properties. Using MD, DFT, and dislocation analysis, researchers have demonstrated how HEA coatings effectively mitigate crack propagation, enhance hardness through solid solution strengthening, and reduce wear volume loss for various cutting-edge applications. The insights from MD simulations demonstrate the atomic-scale mechanisms underpinning these improvements, such as strain distributions and dislocation interactions. DFT simulations further reveal the critical role of charge redistribution, orbital hybridization, and covalent bonding in reinforcing heterojunction stability, thereby enhancing mechanical and tribological performance.

In addition to their tribological applications, HEAs exhibit significant catalytic potential, particularly, for example, in electrocatalytic reactions that use water splitting, where elements such as Mo enhance electron transport and catalytic activity. This multi-faceted functionality positions HEA coatings as a transformative material for advanced engineering and industrial applications. With the increased use of HEA coatings and advancements in theoretical understanding of these coatings, the field holds immense promise for expanding computational techniques to study a plethora of unexplored properties and novel compositions and microstructures. For example, nitride and carbide-based HEA coatings present new frontiers for investigation, where their unique properties can be analyzed using MD and DFT. A table summarizing recent advances on elucidation of various properties and the mechanisms of HEA coatings using MD and DFT simulations is provided in Table 5.1.

Furthermore, the incorporation of Monte Carlo simulations [75], which remain underexplored, offers an innovative avenue to model stochastic processes and atomic-scale interactions within HEA coatings enabling more comprehensive predictions of their performance. By combining these advanced methodologies, the future of HEA coating research promises deeper insights and broader applications, pushing the boundaries of multicomponent alloy coatings.

Table 5.1: Summary of recent advances in the elucidation of various properties of HEA coatings using MD and DFT simulations.

Sr. No	Property	Composition of HEA Coating	Technique Used	Remarks
1	Wear Resistance	FeNiCrCoCu [47], AlCoCrFe [44], AlCoCrCuNiTi [73], AlCoCrFeNi [45], FeCoNiCrMo [56], FeCoCrNiMoNb [55]	Molecular Dynamics (MD) [44, 45, 47] Density Functional Theory (DFT) [55, 56, 73]	The wear resistance of HEA coatings is significantly influenced by their composition and microstructural characteristics. Superior wear resistance of HEA coatings is attributed to their ability to absorb mechanical stress, maintain structural integrity under abrasive conditions, and form stable reinforcing phases that enhance hardness and reduce friction.
2	Hardness	AlCoCrFe [44], FeCoCrNiMoNb [55]	Molecular Dynamics (MD) [44, 55]	HEA coatings significantly enhance surface hardness through high modulus, solid solution strengthening, and fine microstructural features, offering superior mechanical protection and wear resistance
3	Catalysis	CoCrFeNiMo [74], CoCrFeNiAl [74]	Density Functional Theory (DFT) [74]	HEA Coating demonstrates exceptional bifunctional electrocatalytic performance, attributed to its porous structure, enhanced electron transfer, and synergistic elemental effects

4	Dislocation / Deformation Behaviour	CuNiAlCoFe [52], FeCoCrNiCu [36], MoWCoTaZr [51]	Molecular Dynamics (MD) [36, 51, 52]	HEA Coatings exhibit strain hardening due to dislocation evolution, stacking faults, and dislocation interactions, contributing to their enhanced mechanical performance under nanoindentation
5	Coefficient of Friction (COF)	FeCoNiTi [46], FeCoNiCrMo [56]	Molecular Dynamics (MD) [46, 56]	The coefficient of friction (COF) of HEA coatings is influenced by interface stability, atomic structure, and microstructural transformations, with the correlation between charge state, friction, and wear rate highlighting the complex interplay of atomic interactions, phase stability, and mechanical performance in the coatings.
6	Strengthening Mechanism	AlCoCrFeNiMo _{0.8} –TiC [70]	Density Functional Theory (DFT) [70]	The primary strengthening mechanism in the HEA composite coating is precipitation strengthening significantly enhancing both strength and hardness.
7	Corrosion Behaviour	(FeCoNi) _{75-x} Cr _x B ₁₅ Si ₁₀ [58], Cu–Mo co-doped CoCrFeNi [57]	Density Functional Theory (DFT) [57, 58]	HEA coatings exhibit enhanced corrosion resistance due to the formation of stable, protective passive films, with certain elements playing key roles in reducing defect density, promoting passivation, and improving electrochemical stability.

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