ATOMIC-SCALE ANALYSIS OF MECHANICAL AND WEAR PROPERTIES OF FeNiCoCuPd HIGH-ENTROPY ALLOYS COATING ON Cu SUBSTRATE

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Abstract - This study investigates the influence of an FeNiCoCuPd high-entropy alloy (HEA) coating on a copper substrate under scratch conditions. The results demonstrate that the HEA coating significantly enhances the surface mechanical properties of the substrate. The interface between the coating and the substrate acts as an effective barrier, confining phase transformations. The generation and propagation of dislocations primarily within the HEA coating layer. Furthermore, an increase in coating thickness leads to a reduction in the coefficient of friction. The coating layer effectively bears the majority of the applied stress and plastic deformation, impeding the extensive propagation of stress and dislocations into the substrate, thereby mitigating significant damage. The enhanced protective effect observed with increasing coating thickness, correlated with higher applied forces and a larger stressed volume within the coating, underscores the crucial role of such thin film coatings in improving the surface hardness and wear resistance of metallic substrates.

Key words - Mechanical properties; wear characteristics; high-entropy alloys; coatin

1. Introduction

High-entropy alloys (HEAs), a novel class of metallic materials containing five or more principal elements in equimolar or near-equimolar ratios, have attracted significant attention in materials science [1-5]. Unlike conventional alloys, HEAs tend to form simple solid-solution phases with face-centered cubic (FCC), body-centered cubic (BCC), or a mixture of FCC and BCC structures, rather than complex intermetallic compounds. This unique characteristic, coupled with sluggish diffusion, severe lattice distortion, and cocktail effects, enables HEAs to demonstrate exceptional properties, including high wear resistance, superior hardness, and good ductility [6-12].

The remarkable properties of HEAs make them promising candidates for various applications, particularly as protective coatings to enhance the surface performance of structural materials. By applying HEA coatings, the wear resistance of components can be significantly improved, thereby extending their service life. Various coating techniques have been employed to fabricate HEA coatings, such as laser coating, magnetron sputtering, detonation spraying, plasma cladding, and electrochemical deposition.

Among the vast family of HEAs, the FeNiCoCuPd alloy has emerged as a material of interest due to its potential for achieving enhanced surface protection. While conventional HEAs like AlCoCrFeNi have been extensively studied, FeNiCoCuPd offers a distinct compositional variation that may yield unique mechanical and tribological behaviors [13, 14].

The application of HEA coatings on substrates like copper (Cu) is of particular interest for enhancing surface durability. Cu is widely used in various industrial applications due to its excellent electrical and thermal conductivity. However, its relatively low hardness and wear resistance limit its use in harsh tribological environments. Coating Cu with a high-hardness HEA layer can effectively address these limitations.

In this study, we investigate the influence of FeNiCoCuPd HEA coating thickness on the deformation behavior and wear mechanisms of Cu substrates under scratch conditions. Understanding the relationship between coating thickness and scratch resistance is crucial for optimizing the design of protective coatings and predicting their performance in service. Molecular dynamics (MD) simulations are employed to provide atomic-level insights into the scratch behavior, allowing for a detailed analysis of the underlying deformation and wear mechanisms.

2. Model and Method

The molecular dynamics (MD) simulations were conducted using the model illustrated in Figure 1. The simulation cell consisted of a substrate with dimensions of 200 Å (L) x 120 Å (W) x 160 Å (H) along the x, y, and z axes. The substrate was modeled using copper (Cu) atoms. A high-entropy alloy (HEA) coating, composed of an equiatomic mixture of iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), and palladium (Pd) atoms, was deposited onto the Cu substrate. The coating thickness (t) was systematically varied to analyze its effect on scratch behavior. Simulations were performed with t values of 0 Å (representing pure Cu), 10 Å, 15 Å, 21 Å, and 28 Å. A spherical diamond indenter with a radius of 35 Å was employed to simulate the scratching tool.

The MD simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [15]. Initially, the atomic model underwent energy minimization using the conjugate gradient algorithm to eliminate any unfavorable high-energy configurations. Following minimization, the system was equilibrated under an NPT (constant number of particles, pressure, and temperature) ensemble at 300 K for 100 ps to achieve thermal equilibrium at the target temperature. A time step of 1 fs was used for all simulations.

After equilibration, a scratch test was simulated by moving the diamond indenter across the surface of the sample. The indenter was driven to a penetration depth of 10 Å, and the scratching process was performed over a distance of 150 Å along the x-direction. The interactions between the Cu and HEA atoms were described by the embedded atom method (EAM) potential [16], while the interaction between the indenter and the substrate atoms was modeled using the Lennard-Jones (L-J) potential [17]. For computational efficiency, the diamond indenter was treated as a rigid body.

The resulting atomic trajectories were analyzed to investigate the deformation behavior and wear mechanisms during the scratch process. The atomic configurations were visualized using the Ovito software package [18]. Further analysis included structural characterization by calculating the adaptive centrosymmetry parameter (CSP). Dislocation development within the material was quantified using the dislocation extraction algorithm (DXA).

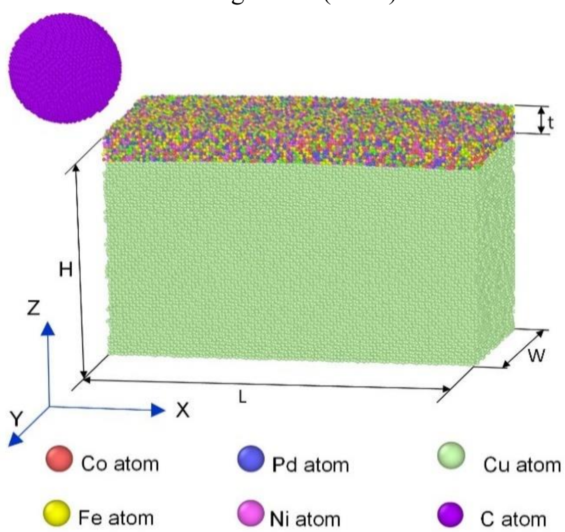

Figure 1. *The simulation model used to study the nanoscratching of a FeNiCoCuPd high-entropy alloy coating on a Cu substrate*

3. Results and discussion

Figure 2 presents a series of snapshots illustrating the nanoscratching process of a pure Cu substrate and Cu substrates coated with a FeNiCoCuPd high-entropy alloy (HEA) at varying coating thicknesses. The left column (a1-e1) displays the initial, un-scratched configurations (scratch length, L = 0 Å), while the right column (a2-e2) shows the configurations after a scratch length of 150 Å, at a scratch depth of 10 Å, a scratching velocity of 50 m/s, and a temperature of 300 K (room temperature). The results indicate a clear trend: as the thickness of the FeNiCoCuPd HEA coating increases, the resistance of the Cu substrate to the nanoscratching process improves. This is evidenced by the decreasing groove depth and reduced material pile-up with increasing coating thickness. The pure Cu substrate exhibits the most significant deformation and material removal, while the thickest HEA coating (28 Å) provides the most effective protection.

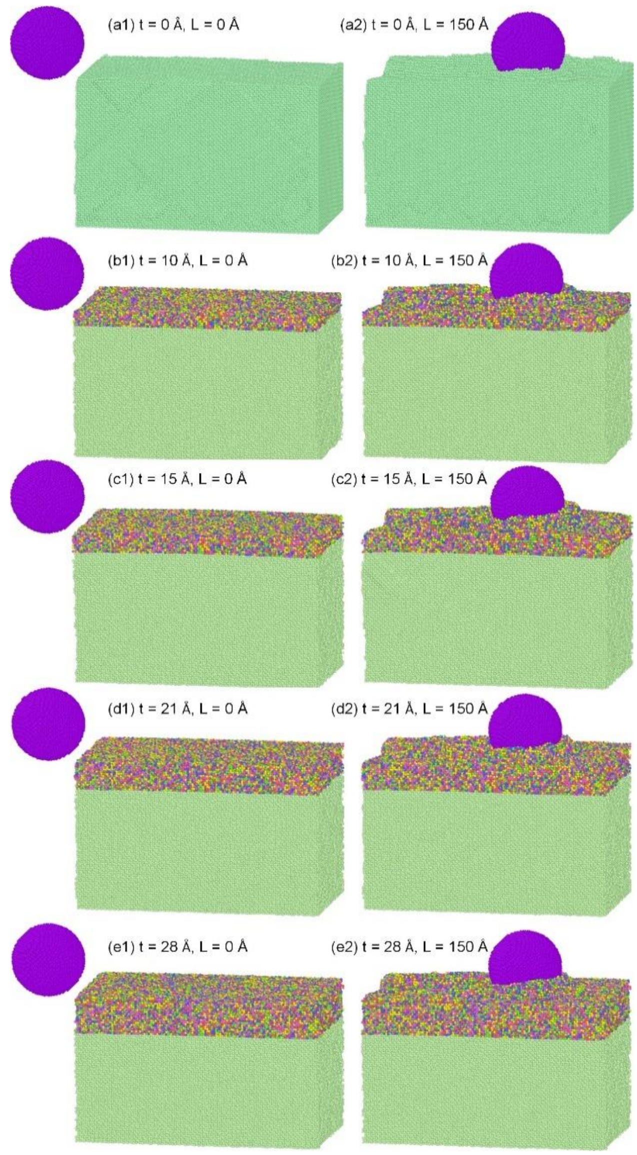

Figure 2. *Scratch process with different coating thicknesses: (a) pure Cu, (b) coating thickness 10 Å, (c) t = 15 Å, (d) t = 21 Å, (e) t = 28 Å.*

Figure 3 illustrates the normal and tangential forces as a function of the HEA coating thickness. The tangential and normal forces are defined as the total of all forces acting on the cutting tool atoms along the X-direction and Z-direction, respectively.

During the initial scratching stage, the machining force develops and gradually increases as the cutting tool makes contact with the workpiece. This increase is attributed to the expanding contact area, which elevates the resistance of the workpiece atoms to the cutting tool, thereby leading to a rise in the machining force with increasing scratch distance. The scratching force stabilizes, exhibiting fluctuations in the force curves, when the cutting distance exceeds 35 Å. These force fluctuations arise from the continuous generation and annihilation of dislocations during the deformation process. Notably, the tangential force maintains a relatively stable value during steady-state scratching, reflecting its role in sustaining a constant rate of material removal during the cutting process.

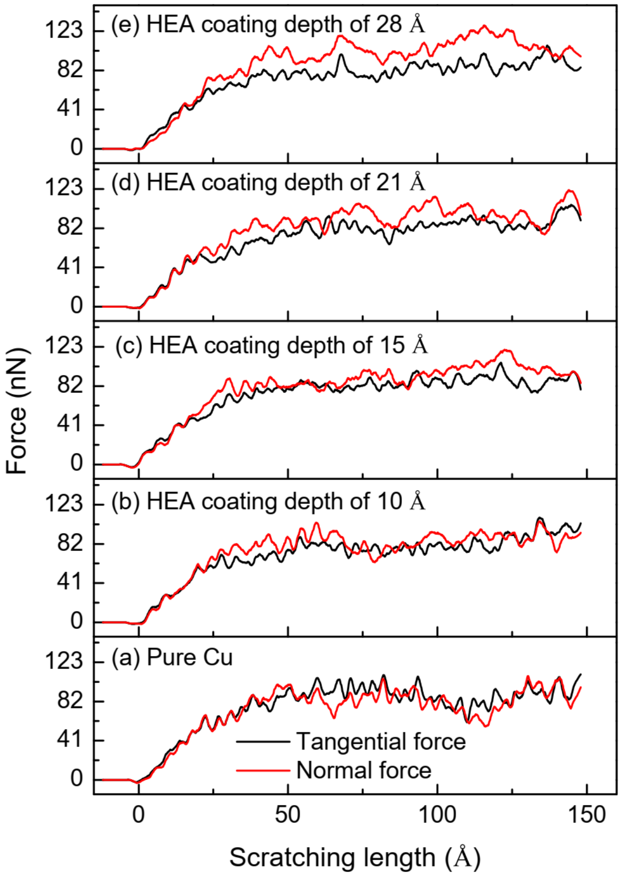

***Figure 3.** Normal and tangential forces at different coating thicknesses*

To compare the force values across different coating thicknesses, the average forces during the stable scratching regime (from 35 Å to 150 Å) were calculated, as shown in Figure 4a. The results in Figure 4a reveal that the pure Cu substrate exhibits the highest tangential force (Fx = 88.9 nN). With the application of the HEA coating, the tangential force tends to stabilize around 84 nN. This observation correlates with the results in Figure 2, where the pure Cu case displays the largest pile-up height, resulting in the highest resistance force (Fx). Conversely, the normal force (Fz) demonstrates an increasing trend with increasing coating thickness. Specifically, the normal force values for pure Cu, t = 10 Å, t = 15 Å, t = 21 Å, and t = 28 Å are 84.5 nN, 85.9 nN, 94.1 nN, 95.6 nN, and 105.2 nN, respectively. This finding suggests that increasing the coating thickness enhances the surface stiffness, indicating an improvement in the surface mechanical properties of the substrate due to the HEA coating.

The coefficient of friction of the material surface is defined as the ratio of the tangential force to the normal force. Figure 4b shows that the friction coefficient decreases as the coating thickness increases. This indicates that the coating contributes to both enhanced mechanical properties and reduced friction coefficient of the material. These results suggest the potential application of such coatings for improving the surface mechanical properties of metallic substrates.

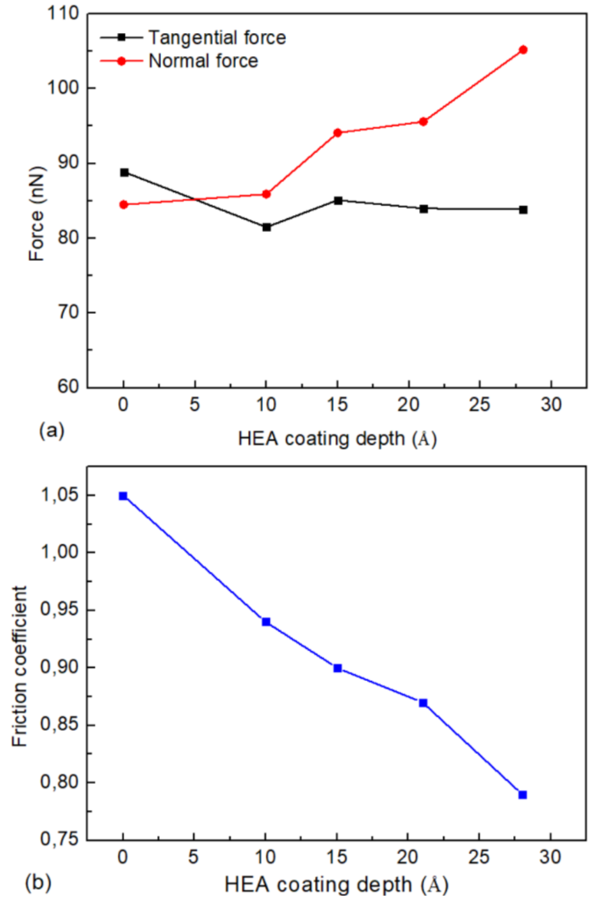

***Figure 4.** Average force and friction coefficient for different HEA coating thicknesses*

Figure 5 presents the distribution of von Mises stress (VMS), structural changes, and dislocation distribution of the substrate during the scratching process with varying coating thicknesses. The results in Figure 5 (a1-e1) demonstrate that the von Mises stress (VMS) is highest at the front and beneath the tool during the scratching process. As the coating thickness increases, the region of high VMS also expands. This can be attributed to the increase in the force along the z-direction (Fz) with greater coating thickness, leading to an increase in VMS. Notably, the stress is primarily concentrated in the coating region, indicating that the interface between the coating and the substrate acts as a barrier, preventing the propagation of stress and deformation into the substrate. Figure 5 (a2-e2) illustrates the structural changes of the substrate during the scratching process. When the coating is present, the structural changes mainly occur within the coating rather than spreading into the substrate. This further confirms the protective role of the coating, minimizing structural alterations in the underlying Cu substrate. Figure 5 (a3-e3) shows the distribution of dislocations during the scratching process with different coating thicknesses. The results indicate that in the case of pure Cu (without coating), dislocations can easily propagate throughout the substrate, leading to its deformation. In contrast, with the presence of a coating, the interface between the coating and the substrate prevents the propagation of dislocations and phase transitions. Dislocations primarily appear beneath the tool and within the coating region, reinforcing the protective role of the coating for the substrate. Figure 5 shows that the coating not only reduces stress concentration within the substrate but also limits structural changes and dislocation distribution, serving as an effective protective layer for the Cu substrate.

Crucially, the analysis reveals that as the coating thickness increases (from (a1) to (e1)), the region exhibiting high VMS also expands. This observation aligns with the provided information that an increase in coating thickness leads to a higher normal force acting on the surface, consequently resulting in elevated von Mises stress levels within a larger volume of the material.

Furthermore, the stress concentration is predominantly observed within the coating layer itself. This suggests that the interface between the coating and the substrate acts as a significant barrier, impeding the transmission of stress and deformation into the underlying substrate. The coating effectively bears the brunt of the applied load and the associated stresses.

Figures 5(a2) through (e2) depict the microstructural changes occurring within the material as the scratch progresses for different coating thicknesses. These images likely visualize atomic displacements or other structural indicators that reveal the extent of plastic deformation and material pile-up.

The images visually corroborate the findings from the stress analysis. In the case of pure copper (a2), the deformation appears to extend more deeply and uniformly into the substrate. However, with increasing coating thickness (b2-e2), the deformation seems to be more localized within the coating layer, with less apparent disruption of the substrate's structure. This reinforces the protective role of the coating in shielding the substrate from significant plastic deformation.

Figures 5(a3) through (e3) illustrate the distribution of dislocations within the material after the scratch. Dislocations are line defects in the crystal lattice that are the primary carriers of plastic deformation in metals. Their distribution provides valuable insights into the mechanisms of material removal and damage accumulation.

The results presented in these figures provide further evidence supporting the previous observations. In the pure copper case (a3), dislocations are seen to propagate relatively easily throughout the substrate, indicating widespread plastic deformation. This explains the higher susceptibility of the uncoated material to scratching.

In contrast, when a coating is present (b3-e3), the interface between the coating and the substrate effectively hinders the transmission of both phase transformations and dislocations. The majority of dislocations are concentrated beneath the indenter and within the coating layer. This localization of dislocations within the coating demonstrates its role as a protective layer, absorbing much of the plastic deformation and limiting damage to the substrate.

The results presented in Figure 5 provide compelling evidence for the protective effect of a thin film coating on a copper substrate during a scratch test. The analysis of von Mises stress distribution, microstructural evolution, and dislocation behavior consistently demonstrates that the coating layer bears the majority of the applied stress and plastic deformation. The interface between the coating and the substrate acts as a barrier, preventing the extensive propagation of stress and dislocations into the substrate, thereby safeguarding it from significant damage. As the coating thickness increases, this protective effect appears to become more pronounced, correlating with higher applied forces and a larger volume of stressed material within the coating. These findings highlight the crucial role of thin film coatings in enhancing the surface hardness and wear resistance of metallic substrates.

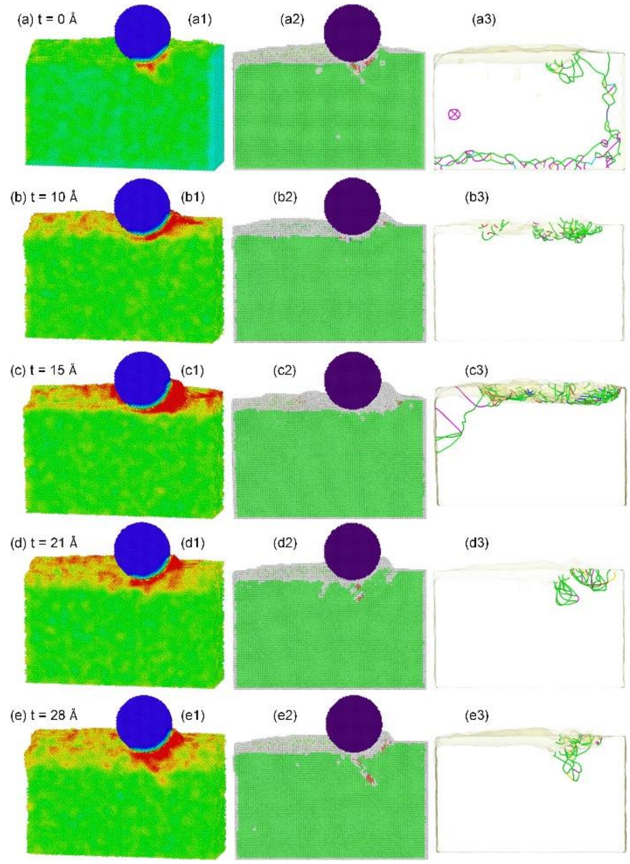

Figure 5. *Distribution of von Mises stress (a1-e1), structural changes (a2-e2), and dislocation distribution (a3-e3) of the substrate during scratching at a length of 150 Å with different coating thicknesses*

4. Conclusion

The present study investigated the impact of a High-Entropy Alloy (HEA) coating with varying thicknesses on the scratch behavior of a pure copper (Cu) substrate. Our findings reveal a significant influence of the HEA coating on both the mechanical response and frictional characteristics during the scratch process. Notably, the pure Cu substrate exhibited the highest tangential force (F_x =88.9 nN), while the application of the HEA coating led to a stabilization of the tangential force around 84 nN. Conversely, the normal force (F_z) displayed an increasing trend with increasing coating thickness, with values of 84.5 nN, 85.9 nN, 94.1 nN, 95.6 nN, and 105.2 nN observed for pure Cu, t=10 Å, t=15 Å, t=21 Å, and t=28 Å, respectively. This increase in normal force with coating thickness underscores the enhanced load-bearing capacity provided by the HEA layer.

Furthermore, a reduction in the coefficient of friction was observed with increasing coating thickness, indicating that the HEA coating contributes to both improved mechanical properties and a lower frictional response of the material. The analysis of the von Mises stress distribution, microstructural evolution, and dislocation behavior consistently demonstrated the protective effect of the thin film coating on the copper substrate during the scratch test. The coating layer effectively bears the majority of the applied stress and plastic deformation, with the interface between the coating and the substrate acting as a barrier that impedes the extensive propagation of stress and dislocations into the substrate, thereby mitigating significant damage. The enhanced protective effect with increasing coating thickness, correlated with higher applied forces and a larger stressed volume within the coating, further highlights the crucial role of thin film coatings in enhancing the surface hardness and wear resistance of metallic substrates. These results strongly suggest the potential application of such HEA coatings for improving the surface mechanical properties of metallic substrates in tribological applications.

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