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A molecular dynamics study on the Mie-Grüneisen equation-of-state and high strain-rate behavior of equiatomic CoCrFeMnNi

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ABSTRACT

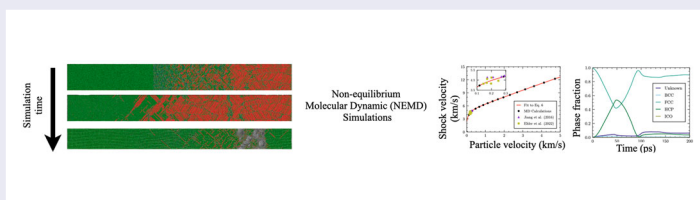
Through atomistic simulations, we uncover the dynamic properties of the Cantor alloy under shock-loading conditions and characterize its equation-of-state over a wide range of densities and pressures along with spall strength at ultra-high strain rates. Simulation results reveal the role of local phase transformations during the development of the shock wave on the alloy's high spall strength. The simulated shock Hugoniot results are in remarkable agreement with experimental data, validating the predictability of the model. These mechanistic insights along with the quantification of dynamical properties can drive further advancements in various applications of this class of alloys under extreme environments.

ARTICLE HISTORY

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KEYWORDS

Spall; equation of state; high entropy alloys; phase transformation; atomistic simulations



IMPACT STATEMENT

The spall behavior of Cantor alloys is mediated by a strain-rate dependent, reversible FCC-to-HCP phase transition mechanism during shock loading endowing them with high spall strength compared to conventional alloys.

1. Introduction

High-performance materials that tolerate high temperatures, pressures, and deformation rates beyond contemporary engineering design conditions are attracting an ever-increasing demand in the search for ensuring safety, enhancing performance, improving energy efficiency, and reducing costs in various industries [1–7]. Of particular interest is the equiatomic CoCrFeMnNi high-entropy alloy (HEA), also known as the Cantor alloy, as a structural material in barrier coating applications where thermo-mechanical shocks or corrosive substances are present [8]. Understanding the high strain-rate and spallation behavior of this HEA in these environments necessitates the characterization and quantification of multiple fundamental properties, including equation-of-state (EOS), constitutive

relationships, microstructure evolution, and dynamic deformation mechanisms. These properties describe the material's behavior under changes in pressure, volume, entropy, and temperature, making them fundamental to the design of novel materials that share similar structural and chemical features capable of withstanding extreme mechanical environments.

Experimental investigations into a material's EOS and spall strength typically involve the use of a gas gun, high-power laser, or explosive drivers capable of accessing strain rates up to 10^8 s^{-1} to shock compress a specimen to some increased pressure state [9–11]. These techniques are routinely utilized with in-situ gauges for shock velocity and stress state measurements or interferometry methods such as Photon Doppler Velocimetry (PDV) [12], Velocity Interferometer System for Any Reflector

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(VISAR) [13], or Optically Recording Velocity Interferometer System (ORVIS) [14] to measure the velocity profile of the shocked free surface. Data from these experiments allows for the determination of parameters defining the material's dynamic response via known thermodynamic relationships. For example, Jiang et al. [15] used a gas gun and PDV to investigate the shock Hugoniot in the shock velocity (U_s) versus particle velocity (U_p) space, the Hugoniot elastic limit (HEL), and the phase transition threshold stress of equiatomic CoCrFeMnNi at strain rates in the 10^6 s^{-1} range. They attributed the relatively high HEL and phase transition threshold stress in this HEA to its intrinsic chemically disordered structure. Likewise, Thürmer et al. [16] employed a pulsed-laser setup to shock polycrystalline CoCrFeMnNi samples in the 10^7 s^{-1} range combined with VISAR measurements of the free surface velocity to extract spall strengths from characteristic pull-back signals. They showed that the high spall strength of this HEA may originate from a homogeneous composition, an absence of second-phase particles and/or segregation at grain boundaries, and a high density of nanotwins near the spall plane. Most recently, Ehler et al. [17] utilized laser-launched Al flyers and PDV to explore both the EOS and spall strength of additively manufactured CoCrFeMnNi samples at strain rates in the 10^6 s^{-1} range, and concluded that the failure mechanisms behind spallation occurred via ductile fracture at voids presumably created during manufacturing.

Modeling and simulation methods are also being leveraged, primarily at the atomistic length scales with density functional theory (DFT) [18,19] and molecular dynamics (MD) [20–22]. These efforts generally aim to address fundamental properties at the microscale (e.g., crystal structure, magnetic states, defects, phase transitions) that influence macroscopically observable quantities of interest (e.g., plastic deformation, fracture strength, spallation). For example, Ma et al. [23] carried out finite-temperature DFT calculations to investigate the equilibrium structures, stability, and magnetic moments of the FCC, BCC, and HCP CoCrFeMnNi phases up to 1200 K and highlighted the role of configurational, vibrational, electronic, and magnetic entropy contributions. Choi et al. [24] performed MD simulations of single-crystal CoCrFeMnNi to investigate its slow vacancy diffusion, twin formation under uniaxial tension, and critical resolved shear stress. Thürmer et al. [16] utilized MD to simulate shock loading of equiatomic CoCrFeMnNi by a piston impactor to study damage production and structural morphology behind traveling shock waves in addition to the spall strength at strain rates up to 10^9 s^{-1} . Similarly, Liu et al. [25] used MD simulations to examine the effect of crystallographic orientation on both the shock

Hugoniot in $U_s - U_p$ space and dislocation formation in equiatomic CoCrFeMnNi under shock loading conditions.

In this work, we are interested in expanding upon these previous studies to develop a comprehensive understanding of the dynamic behavior for equiatomic, single-crystal CoCrFeMnNi by investigating (i) the EOS for a wide range of densities and pressures and (ii) the spallation behavior at high strain-rates. MD simulations were performed to map out the principle shock Hugoniot, which is shown to agree remarkably well with available experimental data. We have also calculated the Grüneisen parameter and constant-volume specific heat to generate a Mie-Grüneisen type EOS that captures low-pressure non-linearities predicted by our MD simulations. Non-equilibrium MD (NEMD) simulations of shock compression were performed for a range of impactor velocities with strain rates around 10^9 s^{-1} . We calculated the spall strength from these simulations as a function of the strain rate via pull-back signals obtained by measuring the free surface velocity during shock compression and release. Additionally, local lattice structures were calculated to elucidate phase transformation details during the shock-loading and spallation processes. These mechanistic understandings provide valuable insights into the factors that affect spall behavior in a wide range of alloys that share similar crystallographic structure and chemical features. This knowledge can be used to design new alloys with improved spall resistance for a variety of applications.

2. Methods

We used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code to perform MD simulations of CoCrFeMnNi [26,27]. The second nearest-neighbor modified embedded atom method (2NN-MEAM) interatomic potential developed by Choi et al. [24] was used to model CoCrFeMnNi. We chose this potential based on previous successes to study various mechanical properties of CoCrFeMnNi, including micro-twinning during tensile deformation of crystalline samples [24], strain-induced phase transformations in nanocrystalline samples [28], elastic responses and dislocation formation during nanoindentation [29], and high strain-rate compression and spallation [16]. The equiatomic single-crystal structures were created by randomly distributing the CoCrFeMnNi atoms on a FCC lattice in equal ratios of 20% with a lattice constant of 3.592 Å, which corresponds to the theoretical maximum density determined experimentally by Melia et al. [30] of $\rho_0 = 8.036 \text{ g/cm}^3$. Note that there is a range of experimentally determined lattice constants between

3.59 Å (8.051 g/cm³) and 3.604 Å (7.957 g/cm³) [30–35]. As the shock Hugoniot strongly depends on the reference state's density, the above lattice constant was found to be a reasonable median value, within experimental accuracies, to characterize the EOS for the CoCrFeMnNi alloy considered here. Since CoCrFeMnNi has a random atomic configuration, we created 10 structures, each with different configurations, for every MD simulation to elucidate any dependencies on such atomic disorder and report the averaged results.

To calculate the Hugoniot, we used a cubic simulation domain with edge lengths of 17.985 nm, containing 500,000 atoms, as the reference specific volume, $V_0 (= 1/\rho_0)$. Points on the Hugoniot were determined via a method similar to that of Chantawansri et al. [36], which requires a series of canonical-ensemble (NVT) simulations be performed with specific volumes, V , that are less than the reference specific volume, *i.e.*, $V < V_0$. A series of structures were isotropically strained in increments of 1% and equilibrated to 300 K for 100 ps using periodic boundary conditions and a 1 fs time step. The temperature of these structures was then ramped from 300 K to some higher temperature that depended on the level of strain to ensure the Hugoniot temperature was bracketed by the initial and final temperatures (*e.g.*, 400 K for $V/V_0 = 0.99$ and 50,000 K for $V/V_0 = 0.85$). Simultaneously, time-averaged thermodynamic quantities were recorded every 1 ps for 100 ps. The Rankine-Hugoniot relationship for energy conservation [9] was evaluated for these data points to produce residual values, δ_H , as a function of the temperature, T , via

$$\delta_H(T) = E(T) - E_0 + \frac{1}{2} [P(T) + P_0] [V - V_0], \quad (1)$$

where E , P , and V are the internal energy, pressure, and specific volume, respectively, of the compressed state. The subscript '0' denotes the same quantities for the initial, uncompressed reference state. The temperature at which Equation (1) is zero determines the Hugoniot temperature and thereby the Hugoniot pressure. Experimental Hugoniot data is often reported in terms of the shock velocity, U_s , and the particle velocity, U_p . We obtained these values from the following relationships [9]

$$U_s = \sqrt{V_0 (P - P_0) / (1 - V/V_0)}, \quad (2)$$

and

$$U_p = \sqrt{V_0 (P - P_0) (1 - V/V_0)}, \quad (3)$$

where V is a given specific volume and P is the corresponding Hugoniot pressure as determined above.

We performed NEMD simulations of shock compression in CoCrFeMnNi using a domain with dimensions

29.8551 nm × 29.8551 nm × 299.9898 nm containing 22,995,482 atoms. Shock loading by a (momentum mirror) piston with velocity u_0 occurred along the [001] crystallographic direction (*i.e.*, the +Z-axis). We considered piston velocities between 0.25 km/s and 2.00 km/s in 0.25 km/s increments. Prior to these simulations, structures were equilibrated to 300 K and 0 bar using the isothermal-isobaric (NPT) ensemble for 100 ps with a 1 fs timestep. During the shock simulations, we used the microcanonical (NVE) ensemble with a 1 fs timestep. Dimensions perpendicular to the shock-loading direction were periodic and held fixed, while the shocked surface and free surface were both non-periodic and shrink-wrapped to encompass any shock-induced movement. To facilitate analysis of these NEMD simulations, several thermodynamic quantities were tracked in the direction of the shock (*i.e.*, Z-axis), below the impacted surface. A series of slabs were created along the Z-axis by spatially dividing the domain into 10 nm bins. For each bin, the average density, Z-component of the material velocity, per-atom stress tensor, and per-atom Voronoi volume were computed. Analogous to interferometry methods, the average velocity of a 1 nm thick slab at the free surface was tracked to elucidate spall strengths via pull-back signals [16,37,38]. The local lattice structure was calculated for the entire domain via the method of Ackland and Jones [39] in order to track phase transformations during shock wave compression, rarefaction wave relief, and spallation.

3. Results and discussion

Since a single shock wave defines only one (P, ρ) point on the Hugoniot [11], the Hugoniot is represented via a set of (P, ρ) points as illustrated by our principle shock Hugoniot results in Figure 1(a) for CoCrFeMnNi. Although the Hugoniot is defined in $P - \rho$ space, expressing the Hugoniot in $U_s - U_p$ space, as shown in Figure 1(b), is practical as the results are directly comparable to experimental measurements and non-linear material behavior can be elucidated in low-pressure regimes. From Figure 1(b), it is obvious that CoCrFeMnNi exhibits non-linear dynamic behavior at shock pressures below ≈ 22.5 GPa or, equivalently, particle velocities below ≈ 0.5 km/s, which is generally indicative of elastic yielding, strain-rate dependence, and/or other time-dependent phenomena [11]. Above this shock pressure, the Hugoniot exhibits a classical linear relationship. Our Hugoniot predictions agree very well with experimental data from Jiang et al. [15] and Ehler et al. [17], whose particle velocities range from ≈ 0.1 km/s to ≈ 0.3 km/s (shock pressures between ≈ 6 GPa and ≈ 14 GPa), which is within the non-linear regime.

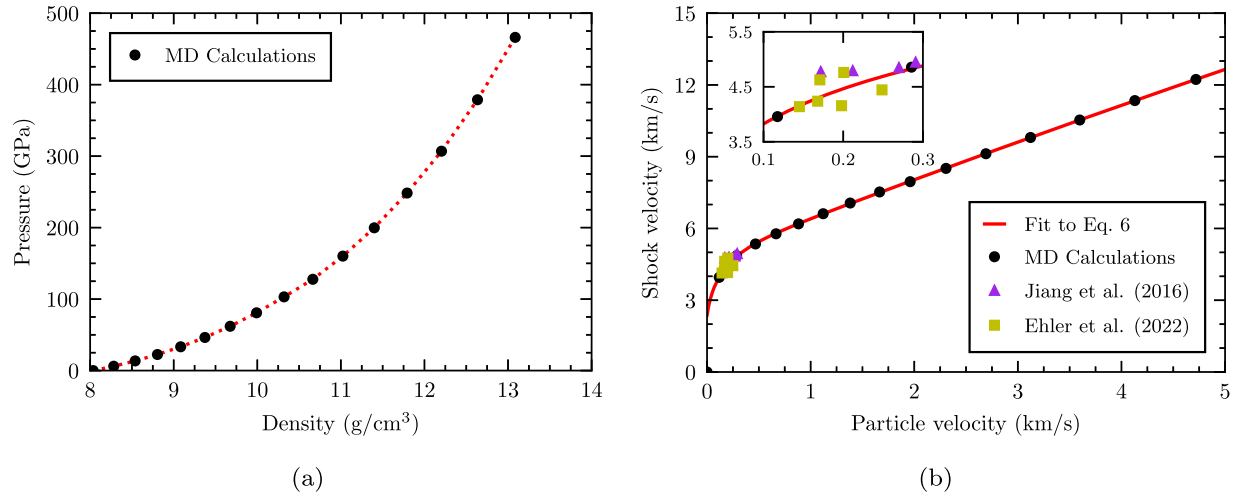


Figure 1. (a) Points on the principle shock Hugoniot in $P - \rho$ space. The dashed red line only serves to indicate the trend of the data. (b) Points on the principle shock Hugoniot in $U_s - U_p$ space along with available experimental data. The solid red line represents the fitted analytic reference curve, Equation (6).

Jiang et al. [15] and Ehler et al. [17] fitted linear $U_s - U_p$ relationships to their data. Since the range of both fitted data sets are narrow and located within the non-linear regime, substantial errors may be incurred describing the shock response of CoCrFeMnNi if these relationships are used in EOS models outside of the fitted range. We fitted an improved $U_s - U_p$ relationship that captures both the predicted low-pressure non-linearity of CoCrFeMnNi and the extent of shock and particle velocities considered to ensure realistic shock descriptions across a wide range of densities and pressures. We have also calculated the Grüneisen parameter, γ_0 , and constant-volume specific heat, C_V , to provide a calibrated Mie-Grüneisen EOS model. These parameters were taken to be constants and were calculated using the reference state at 300 K with the following definitions [9]

$$\gamma_0 = V_0 \left(\frac{\partial P}{\partial E} \right)_V, \quad (4)$$

and

$$C_V = \frac{V_0}{\gamma_0} \left(\frac{\partial P}{\partial T} \right)_V. \quad (5)$$

To relate the T , P , E , and ρ of a shocked material, the Mie-Grüneisen EOS [9] makes use of C_V , γ_0 , and a reference curve, which we have taken to be the $U_s - U_p$ Hugoniot, and is expressed as [40]

$$U_s = 2C_s \left[1 - S_1\mu + \sqrt{(1 - S_1\mu)^2 - 4S_2\mu^2} \right]^{-1} - B \exp \left[- \left(\frac{\mu}{\mu^*} \right)^N \right], \quad (6)$$

Table 1. Calibrated Mie-Grüneisen EOS model parameters. The fitting parameter N was chosen to be fixed at 1.0.

Quantity	Value
Reference density, ρ_0 (g/cm ³)	8.03640
Grüneisen parameter, γ_0	1.75210
Specific heat, C_V (J/g · K)	0.43167
Bulk sound speed, C_s (km/s)	4.78463
Linear coefficient, S_1	1.66206
Quadratic coefficient, S_2	-0.08539
Low-pressure parameter, B (km/s)	2.41519
Low-pressure parameter, μ^*	0.03635
Low-pressure parameter, N	1.0

where C_s is the sound speed in the material at zero pressure, $\mu = U_p/U_s$ is the strain, and the remaining variables are fitting constants. Note that other analytical EOS forms can be used with comparable overall predictions [41].

Non-linear least squares was used to fit Equation (6) to our predicted Hugoniot. Model parameters are summarized in Table 1. As expected, the fitted reference curve captures the simulated Hugoniot and experimental data very well, as shown in Figure 1(b). The bulk sound speed was determined to be ≈ 4.78 km/s. Jiang et al. [15] and Ehler et al. [17] calculated ≈ 4.50 km/s and ≈ 3.97 km/s, respectively; differences of $\approx 6.1\%$ and $\approx 18.6\%$. The Grüneisen parameter and specific heat were calculated via the temperature ramp MD simulations described above and are given in Table 1. We report a value of $\gamma_0 = 1.75210$, which is in good agreement with Jiang et al. [15] who calculated $\gamma_0 = 1.78$ using the Dugdale and Macdonald approximation [42]; a difference of $\approx 1.6\%$.

During the NEMD simulations, a shock wave reflects off of the free surface. This rarefaction wave places

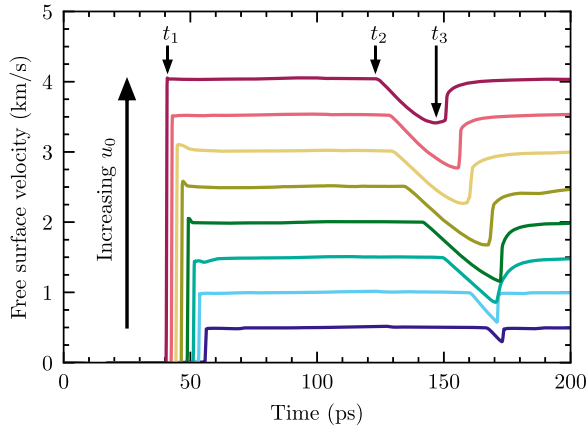


Figure 2. Free surface velocity, u_{fs} , traces for the NEMD simulations.

the shock compressed material into a state of tension. Spallation occurs at some depth below the impacted surface, *i.e.*, the spall plane, when this tensile stress exceeds the material strength [22]. Analysis of this shock-induced spallation was performed by examining the free surface velocity, u_{fs} , as a function of time. Figure 2 shows free surface velocity traces from our NEMD simulations. These traces include the shock arrival time, t_1 , where the free surface acquires a velocity $u_{fs} = 2u_0$, and the pull-back signal between t_2 and t_3 , which is directly correlated to the spallation process. The free surface velocity difference, Δu_{fs} , between t_2 and t_3 was used to calculate the spall strength, σ_{sp} , via [16,17,37,38]

$$\sigma_{sp} = \frac{1}{2} \rho_0 C_s \Delta u_{fs} \quad (7)$$

where ρ_0 is the initial density and C_s is the bulk sound speed.

Table 2 summarizes our calculated spall strengths with the corresponding strain rates for simulations where spall was observed. Predictably, there is a strain-rate dependence in the spall strength where spall strength decreases with increasing strain rate. The spall strengths for piston velocities of 1.50 km/s and 1.75 km/s are quite similar, while an increase or decrease from these piston velocities results in substantial spall strength changes.

Table 2. Strain-rate dependent spall strengths for CoCrFeMnNi calculated using Equation (7).

u_0 (km/s)	Strain rate (s^{-1})	Spall strength (GPa)
0.25	8.466×10^8	–
0.50	1.673×10^9	–
0.75	2.505×10^9	–
1.00	3.330×10^9	–
1.25	4.158×10^9	15.664
1.50	4.991×10^9	13.894
1.75	5.816×10^9	13.807
2.00	6.639×10^9	11.134

Interestingly, the pull-back signal minima for the 4 piston velocities where spall was not observed all occur at $t_3 \approx 172$ ps, while the minima increasingly occur earlier with increasing piston velocity when spall manifested; a feature directly related to material strength. In previous studies, Ehler et al. [17] experimentally determined spall strengths of ≈ 1.64 GPa and ≈ 3.0 GPa with strain rates above $10^6 s^{-1}$. Thürmer et al. [16] experimentally determined a spall strength of ≈ 8 GPa at a strain rate of $\approx 10^7 s^{-1}$, and calculated a spall strength upper limit of ≈ 30 GPa at a strain rate of $\approx 10^9 s^{-1}$ using MD simulations and Grady's [43] spall strength model. These values are substantially lower than those reported here since they correspond to polycrystalline specimens, where some of the spall deformation mechanisms active in single-crystal specimens may be suppressed due to grain boundaries and impurities effects in polycrystals [44,45].

Spallation was observed via inspection of space-time-density plots for each NEMD simulation as illustrated in Figure 3. Density variations in these plots indicated shock wave propagation processes related to compression, rarefaction, tension, and spallation in CoCrFeMnNi. Therefore, quantities such as the shock wave velocity and the spall zone were easily identified. Not observed in Figure 3(a) is the sudden drop in density observed in Figure 3(b) at ≈ 106 ps, which signifies spall initiation. Also shown in Figure 3 are plots of the CoCrFeMnNi phase fraction. During shock compression, the initial FCC structure transitions primarily to the HCP structure, which, in turn, is mostly restored to the FCC phase during release. The fraction of FCC converted to HCP during shock compression, and that remained after release, was inherently dependent on the piston velocity. Furthermore, in the case of spallation, significantly more unknown phases were identified which are mainly attributed to the formation of amorphous regions and new interfaces near the spall zone. Similar phase transformation mechanisms affecting the dynamic response have also been observed in other metallic systems [46,47].

4. Summary and conclusions

Through atomistic simulations, we have calculated the principle shock Hugoniot for equiatomic, single-crystal CoCrFeMnNi, which predicts non-linear behavior below, and linear behavior above, shock pressures of ≈ 22.5 GPa. This theoretical Hugoniot was shown to agree remarkably well with available experimental data. The Grüneisen parameter and constant-volume specific heat were also calculated, and determined to be $\gamma_0 = 1.75210$ and $C_v = 0.43167$ J/g·K, respectively. These parameters, in addition to the Hugoniot, were utilized to generate a Mie-Grüneisen type EOS for a wide range of densities

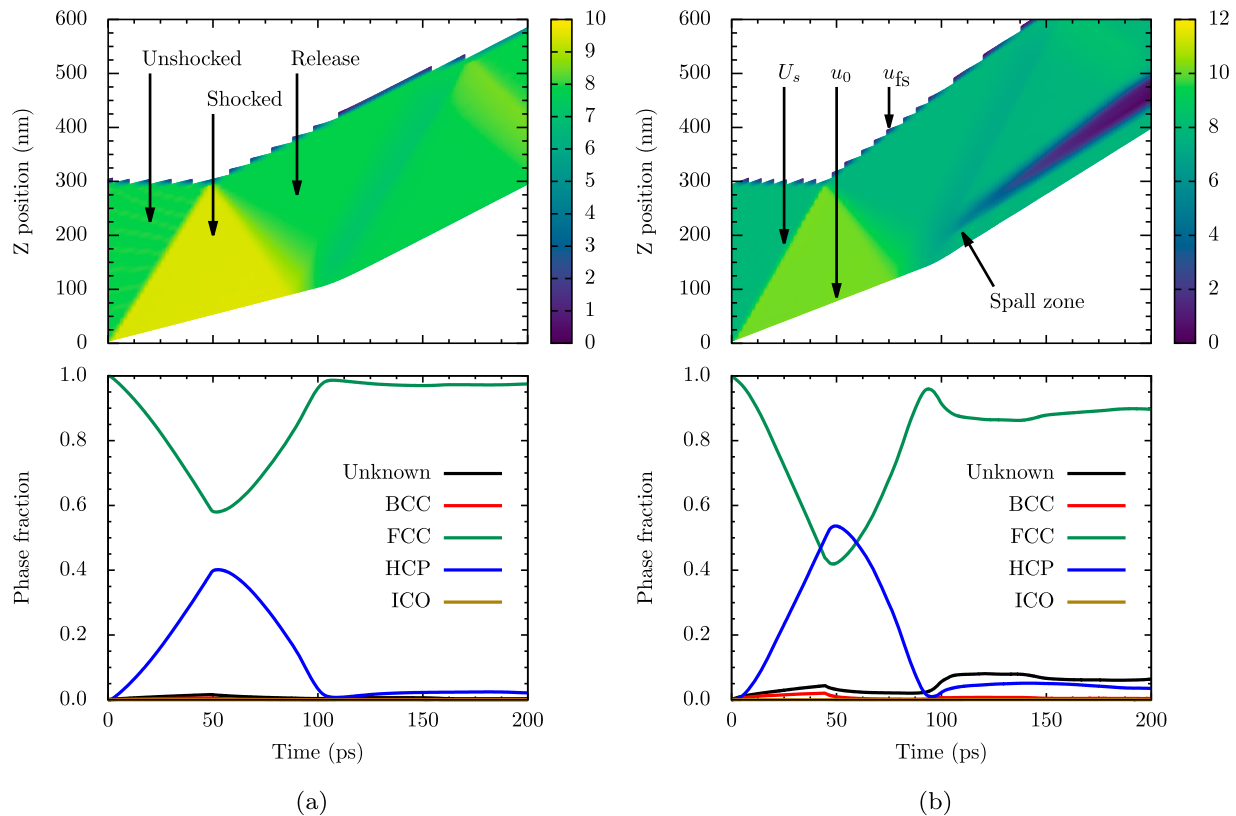


Figure 3. Space-time-density diagrams showing the initial shock wave propagation and subsequent rarefaction waves along with the corresponding phase fraction evolution for (a) no spallation with $u_0 = 1.00$ km/s and (b) spallation with $u_0 = 1.50$ km/s.

and pressures (see Table 1). Additionally, we performed NEMD simulations of shock compression and release for a range of impactor velocities along the [001] crystallographic direction in equiatomic, single-crystal CoCrFeMnNi. To elucidate the strain rate dependent spall strength, free surface velocity analysis was performed. We calculated spall strengths between ≈ 11 GPa and ≈ 16 GPa at strain rates of $\approx 10^9$ s $^{-1}$. Moreover, we have highlighted strain rate dependent FCC $\rightarrow$ HCP phase transitions during shock compression, and HCP $\rightarrow$ FCC relaxation during release. While the specific spall strength values and coefficients for the EOS are unique to the equiatomic composition of the Cantor alloy studied here, it is reasonable to posit that both the high spall-strength and the phase transformation mechanisms reported here extend to near equiatomic compositions and to other HEAs that share similar structural and chemical features as this HEA [48,49].

The EOS and spall strengths reported here are an advancement on the current understanding of the dynamic behavior for CoCrFeMnNi in extreme environments. However, there are limitations and open questions to be addressed:

- Although successful, the interatomic potential utilized here was not directly developed for investigating the dynamic behavior of CoCrFeMnNi. Thus, probing

this potential's properties in these shock compression regimes is crucial for predictive accuracy and reliability.

- The Hugoniot we calculated was for isotropic compression of single-crystal CoCrFeMnNi. Characterizing the Hugoniot response uniaxially, or with polycrystalline specimens, would be advantageous. Similarly, characterizing the spall behavior along different crystal orientations or in polycrystalline specimens would complement the current knowledge base.
- Our Hugoniot and EOS do not consider shock-induced polymorphic phase transitions, which are known to introduce discontinuities in the Hugoniot curve. Thus, the usage of a lookup table, as opposed to an analytic expression, to include such transformations and temperature dependent specific heats would improve the EOS model.

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Data availability

The data that support the findings of this study are available from the authors upon reasonable request.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Statement novelty

We characterize and quantify multiple fundamental properties of Cantor alloys, including equations-of-state (EOS), constitutive relationships, and dynamic deformation mechanisms using atomistic simulations. These properties describe the materials behavior under changes in pressure, volume, entropy and temperature, making them fundamental to the design of novel materials that share similar structural and chemical features capable of withstanding extreme mechanical environments. The spall behavior of Cantor alloys is mediated by a strain-rate dependent, reversible FCC-to-HCP phase transition mechanism during shock loading endowing them with high spall strength compared to conventional alloys. These mechanistic understandings provide valuable insights into the factors that affect spall behavior in a wide range of alloys that share similar crystallographic structure and chemical features. This knowledge can be used to design new alloys with improved spall resistance for a variety of applications.

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