Study on Laser Shock Modulation of Melt Pool in Laser Additive Manufacturing of FeCoCrNi High-Entropy Alloys

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Abstract

With growing interest in Laser Additive Manufacturing (LAM) of High-entropy alloys (HEAs) during most recent years, compositional elements design and process strategies innovation are primary methods to overcome undesirable microstructures and defects. Here we propose a new approach, a novel real-time laser shock modulation of melt pool (LSMMP) to obtain melt pool modifications for yielding HEAs with desired characteristics. LSMMP utilizes a pulsed laser shocking a liquid melt pool caused by a continuous wave laser, enabling non-destructive and real-time modulations for high-performance HEAs. The numerical simulation reveals the convection mechanism of the melt pool in the LSMMP process, and the intervention of the pulsed laser promotes melt pool flow type to convert the Marangoni effect into a multi-convective ring, which accelerates melt pool flow and inhibits columnar crystal growth. Experimental results show the evolution law of the microstructure in the LSMMP process. The microstructure of CrFeCoNi HEAs undergoes a Columnar-Equiaxed Transition (CET), and higher hardness is obtained. Laser shock is demonstrated to be an effective in-situ modulative tool for controlled additive manufacturing.

Full Text

Preamble

Study on Laser Shock Modulation of Melt Pool in Laser Additive Manufacturing of FeCoCrNi High-Entropy Alloys

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Abstract: With growing interest in Laser Additive Manufacturing (LAM) of High-entropy alloys (HEAs) in recent years, compositional element design and process strategy innovation have become primary methods for overcoming undesirable microstructures and defects. Here we propose a novel approach—real-time laser shock modulation of melt pool (LSMMP)—to achieve melt pool modifications that yield HEAs with desired characteristics. LSMMP utilizes a pulsed laser to shock a liquid melt pool created by a continuous wave laser, enabling non-destructive, real-time modulation for high-performance HEAs. Numerical simulation reveals the convection mechanism of the melt pool during LSMMP, showing that pulsed laser intervention promotes a transition in melt pool flow from Marangoni-driven convection to a multi-convective ring pattern, which accelerates melt pool flow and inhibits columnar crystal growth. Experimental results demonstrate the microstructural evolution in the LSMMP process, where CrFeCoNi HEAs undergo a Columnar-Equiaxed Transition (CET) with enhanced hardness. Laser shock is thus demonstrated to be an effective in-situ modulative tool for controlled additive manufacturing.

Keywords: Laser shock; High-entropy alloys; Melt pool; Laser Additive Manufacturing

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1. Introduction

Yeh et al. [1] revolutionized materials design by breaking from the traditional single principal element concept and developing High-Entropy Alloys (HEAs) with excellent performance, ushering in a new era for alloy system development that has attracted extensive attention across fundamental research and engineering manufacturing. However, typical metallurgical defects such as porosity and segregation in conventional as-cast HEAs have limited their potential applications. Brief et al. [2] first demonstrated the feasibility of using Laser Additive Manufacturing (LAM) to produce HEAs with superior mechanical properties compared to as-cast samples. Moghaddam et al. [3] subsequently provided a comprehensive review of LAMed HEAs, showing that various components with smooth, bright surfaces can be successfully manufactured. The many advantages of LAM—including the addition of beneficial elements, regulation of process parameters, and selection of appropriate technologies—have been employed to address these defects. Researchers such as Li et al. [4] have shifted focus from FeCoCrNi-based HEAs to performance enhancement through novel material additions. Zhou et al. [5] fabricated carbon-containing FeCoCrNiC0.05 HEAs via Selective Laser Melting (SLM), achieving a uniform carbon distribution and a single face-centered cubic (FCC) structure without carbide phases under optimal parameters. The pre-mixed powder approach has also extended LAM technology to non-metallic materials; for instance, Hu et al. [6] enhanced the plasticity of Zr-based Bulk Metallic Glass (BMG) by adding Nb with higher thermal diffusivity. Zhu et al. [7] manufactured near-fully dense CoCrFeNiMn HEAs by regulating laser power density, achieving an outstanding combination of high strength and excellent ductility compared to conventional methods. Peyrouzet et al. [8] obtained Al0.3CoCrFeNi HEAs with tensile strength up to 896 MPa and yield strength of 730 MPa by adjusting aluminum content, representing significant improvements over as-cast or wrought counterparts. Nevertheless, realizing the full potential of LAMed HEAs requires not only developing materials with new geometries but also novel AM routes to broaden fabrication capabilities.

The extreme thermal cycling of the melt pool during LAM introduces numerous hazards such as pores, cracks, and large grains. Zhang et al. [9] observed cracks in CoCrFeNiMn HEAs samples under different scanning strategies, a finding also reported by Niu et al. [10]. Many researchers have addressed this challenge through various approaches. Jiang et al. [11] showed that adding 5% Fe-based amorphous reinforcement to AlCoCrFeNi HEAs reduced grain diameter, eliminated texture, and decreased specimen anisotropy. The melt pool cooling rate, a critical factor, directly affects the recrystallization process and resulting HEA properties. Li et al. [12] revealed the nanoscale formation mechanism of microstructures in HEAs rapidly cooled to room temperature through Molecular Dynamics (MD) simulation. Most HEAs prepared by Laser Melting Deposition (LMD) exhibit typical columnar dendrites because the LMD growth rate is lower than SLM, preventing equiaxed crystal formation. Tong et al. [13] found that SLMed CoCrFeNiMn HEAs primarily contain columnar crystals inside the melt pool. Post-processing approaches such as the annealing processes used by Knowles et al. [14] after Direct Metal Laser Sintering (DMLS) and Hot Isostatic Pressing (HIP) applied by Li et al. [4] after SLM can modify microstructures, but these methods are cumbersome and disrupt AM process continuity. However, Tong et al. [15] demonstrated that varying process parameters such as laser power and scanning speed during LAM can directly produce different microstructures, with the ratio of temperature gradient (G) to solidification velocity (R) inside the melt pool being the dominant factor in Columnar-Equiaxed Transition (CET).

In-situ modification of the melt pool to obtain superior structures during LAM is therefore particularly important. Laser Shock Peening (LSP) is an advanced technology that induces high compressive stress on metal component surfaces and enables micro- and nano-level structure control. Hu et al. [16, 17] demonstrated ultrafast direct fabrication of surface metallic nanoarrays using LSP. Here we propose a novel synchronous Laser Shock Modulation of Melt Pool (LSMMP) method that enhances melt pool convection and inhibits columnar crystal growth through an additional pulsed laser during LAM. This extends the work of Tong et al. [15], who used LSP as a post-processing treatment to modify LAMed HEAs. Although pulsed lasers are widely used for property strengthening, to our knowledge no research has investigated a synchronous hybrid additive manufacturing process with laser shocking of the melt pool to directly interfere with the recrystallization process. In this paper, we study the LSMMP action mechanism through combined experimental and numerical simulation approaches, revealing the convection mechanism inside the melt pool under sub-10 nanosecond Joule-scale pulsed laser action and discussing the microstructure evolution law of HEAs produced by LSMMP to demonstrate the ultrafast real-time interference capability of LSMMP in metal laser additive manufacturing.

2.1. Materials and Experiment

The LSMMP process integrates a pulsed laser into a liquid HEAs melt pool produced by a continuous wave (CW) laser, as shown in Fig. 1(a). Substrates of 45# carbon steel (30 mm × 30 mm × 1 mm) were polished and cleaned with ethanol solution to ensure surface cleanliness. The steel composition is primarily iron with: C: 0.42-0.5%; Si: 0.17-0.37%; Mn: 0.50-0.80%; P: \$ \$0.035%; S: \$ \$0.035%; Cr: \$ \$0.25%; Ni: \$ \$0.25%; Cu: \$ \$0.25%. The experimental material consisted of equiatomic CrFeCoNi powder prepared by vacuum atomization with particle sizes of 15-45 m, exhibiting good fluidity and sphericity. Powder morphology and composition analysis are shown in Fig. 1(b) and (c). The single-layer CoCrFeNi powder bed thickness was approximately 1 mm. Experimental equipment included a 1 kW continuous wave (CW) fiber laser (Shenzhen Chuangxin Laser Co., Ltd.) and a sub-10 nanosecond Joule-scale pulsed laser. The SLM process was conducted in a high-purity argon atmosphere at a gas flow rate of 3 L/min with process parameters of 800 W laser power, 20 mm/s scanning speed, and 3 mm spot diameter. The pulsed laser parameters were 3 J laser energy, 10 ns pulse width, 10 Hz repetition frequency, and 2 mm spot diameter. The laser energy density (LED) is defined as SLED = P/A, where P is laser energy and A is laser spot area. The CW laser beam was perpendicular to the substrate, while the pulsed laser beam deviated from vertical by -10°.

Fig. 1. (a) Experimental schematic diagram, (b) the SEM image of CrFeCoNi powder, and (c) the EDS analysis of CrFeCoNi powder.

2.2. Characterization Methods

Samples were characterized through process monitoring, microstructural analysis, phase composition determination, and mechanical property evaluation. A Chronos 1.4 high-speed camera (Kron Technologies, Canada) monitored the manufacturing process, while a NewView™ 9000 Series white light interference 3D profiler (ZYGO, United States) measured sample surface profiles. Cross-sections were polished, cleaned, and corroded with aqua regia (hydrochloric acid:nitric acid = 3:1) for 60 seconds. Microstructural analysis and Energy-dispersive Spectroscopy (EDS) were performed using a BX51 optical microscope (OLYMPUS, Japan) and MIRA3 scanning electron microscope (SEM) (Tescan, Czech Republic). Phase composition of the original CoCrFeNi powder and fabricated samples was determined using a D8 ADVANCE X-ray diffractometer (XRD) (Bruker, Germany) with a scanning range of 20-90° at 5°/min. Mechanical properties were measured using an iNano nanoindenter (KLA-Tencor, United States) with a 50 mN load and diamond indenter tip at the upper, middle, and bottom regions of the cross-section.

2.3. Simulations

Molecular Dynamics (MD) Simulations: A 15 Å radius iron sphere with initial velocity (V0) was used to simulate LSMMP impact based on the following equations [18, 19]:

$$P = \frac{I_0 \tau}{2(1+\alpha)} \quad \text{and} \quad V_0 = \frac{I_0 \tau}{m}$$

where I0 is nominal laser intensity, τ is pulse duration, m is iron sphere mass, P is pressure generated during laser irradiation, and α accounts for plasma thermal energy increase from laser absorption. A typical velocity of 1 km/s was applied, with other speed cases calculated for reference. CoCrFeNi HEAs and the iron sphere were modeled as single crystals with FCC and Body-centered cubic (BCC) structures, respectively, with lattice constants of 3.56 Å and 2.863 Å. The modified embedded atom method (MEAM) was employed using the potential function by Mi et al. [20] for HEAs. NVT ensemble was applied with the melt area heated to 2000 K using a 0.001 ps time step.

Three-Dimensional Numerical Model: A 3D numerical model of laser-melt pool interaction was developed to predict temperature and flow fields during LSMMP. To simplify calculations, the following assumptions were made: (1) plasma and metal vapor are ideal gases; (2) shielding gas effects on the additive process are ignored; (3) computational fluids are laminar, Newtonian, and incompressible.

Conservation Equations: Fluid flow and heat transfer in LAM are governed by mass, momentum, and energy conservation equations [21, 22]:

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0$$

Conservation of momentum:

$$\frac{\partial (\rho \mathbf{V})}{\partial t} + \nabla \cdot (\rho \mathbf{V} \mathbf{V}) = \nabla \cdot (\mu \nabla \mathbf{V}) - \nabla P - \frac{\mu}{K} \mathbf{V} + \rho \mathbf{g}$$

Conservation of energy:

$$\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho h \mathbf{V}) = \nabla \cdot (k \nabla T)$$

where is fluid density, **V** is fluid velocity, t is time, is fluid viscosity, P is pressure, K is isotropic permeability, **g** is gravity, T is temperature, h is material enthalpy, and k is thermal conductivity.

Laser Heat Source: The heat source was modeled as a Gaussian volume heat source [23]:

$$q_{\text{laser}} = \frac{3Q}{\pi H (1 - e^{-3})} \exp\left(-\frac{3(x^2 + y^2)}{R_0^2}\right) \exp\left(-\frac{3z^2}{H^2}\right)$$

where Q is laser power, H is laser heat source height, αabs is material absorption rate, and R0 is effective laser beam radius, with >95% of total energy concentrated within radius R0.

Driving Forces: Recoil pressure was modeled using a widely accepted expression [24]:

$$P_r = 0.54 P_0 \exp\left(\frac{\Delta H_{LV}}{R}\left(\frac{1}{T_{LV}} - \frac{1}{T}\right)\right)$$

where P0 is atmospheric pressure, R is universal gas constant, ΔHLV is vaporization enthalpy, TLV is liquid-gas equilibrium temperature, ΔVLV is specific volume difference between liquid and gas, and VLV is gas specific volume. Surface tension as a function of temperature is [21]:

$$\gamma = \gamma_0 - \frac{d\gamma}{dT}(T - T_0)$$

Marangoni force on the fluid surface is [21]:

$$F_{\gamma - i} = -\frac{\partial \gamma}{\partial x_i}$$

where T is liquid surface temperature, T0 is reference temperature, γ0 is surface tension at T0, Fγ-i is Marangoni force from surface tension gradient in direction i, and the negative sign indicates force opposite to the surface tension gradient direction.

Pulse Pressure: Pulse pressure from nanosecond laser shock impacting the melt pool surface vertically downward was simulated as [25, 26]:

$$P(r) = \frac{P}{\sqrt{2\pi}\sigma_P} \exp\left(-\frac{r^2}{2\sigma_P^2}\right)$$

where r is nominal influence radius, σP is pressure distribution parameter, and P is nominal pressure. The temporal pressure distribution was set much longer than the actual laser shock (10 ns scale) due to computational limitations.

Geometric Model and Boundary Conditions: As shown in Fig. 2 and Video 1 (Supplementary material), the computational domain is 50 mm $\times$ 7 mm $\times$ 10 mm with 0.15 mm grid resolution. A 5 mm fluid region represents HEAs material, and a 5 mm void region represents the atmospheric environment to capture the free surface. The CW laser moves left to right at 8 mm/s. The pulsed laser was applied five times (at 1-1.01 s, 2-2.01 s, 3-3.01 s, 4-4.01 s, and 5-5.01 s, with frequency adjustable as needed). Energy and pressure boundary balance conditions were applied at each boundary. Implicit SOR and VOF algorithms updated free surfaces through custom functions, with boundary conditions imposed until calculation completion.

Fig. 2. The schematic diagram of computational domain.

3.1. Surface Topography

To explore LSMMP evolution, real-time melt pool images were collected for both processes, as shown in Fig. 3 [Figure 3: see original paper] and Video 2 (Supplementary material). Fig. 3(a) records the SLM process, where CW laser input fully melts CoCrFeNi powder, gradually forming a plump melt pool ahead of the solidification zone. In contrast, the LSMMP process exhibits distinct characteristics. Fig. 3(b) shows plasma clusters induced by the pulsed laser, which most importantly drives and alters melt pool convection through shock waves. At 3.12 ms, the melt pool undergoes violent oscillation, transforming from a calm convective state to a rolling state. At 3.87 ms, the melt pool heat source center becomes exposed to air, and the surface area expands after each laser shock, enhancing heat transfer. Surface tension then restores the melt pool to its original state in preparation for the next pulsed laser, consequently altering the solidified shape. 3D profile data confirms these observations. CW laser input creates an arc-shaped melt pool (Fig. 4 Figure 4: see original paper), causing slow heat dissipation. In contrast, Fig. 4(c) shows that LSMMP produces a wider, flatter melt pool profile without damaging the additive process. This morphology indirectly indicates increased cooling rate, as the oscillated melt pool solidifies before returning to its original arc-shaped state.

Fig. 3. Real-time images of melt pool evolution: (a) SLM treatment; (b) LSMMP treatment.

Fig. 4. 3D topography and section profile of melt pool under different processes: (a) SLM and LSMMP 3D profiles; (b) SLM treatment; (c) LSMMP treatment.

3.2. Evolution of Material Flow and Temperature Fields

Melt pool morphology changes contribute to cooling rate variations. A plump melt pool model at the solidification zone front was established for CoCrFeNi HEAs to simulate atomic-level evolution, as shown in Fig. 5 Figure 5: see original paper and (b). Fig. 5(c) demonstrates liquid melt pool oscillation under stress, with obvious top deformation. The shock wave propagates three-dimensionally, and the melt pool quickly recovers. Cross-sectional analysis reveals different melt pool sizes between SLM and LSMMP models (Fig. 5(b) and (c)), with the latter becoming wide and flat after cooling. MD simulation results agree with actual sample 3D profile data, validating the MD approach for understanding LSMMP fundamental mechanisms. The cooling process at different time steps is shown in Fig. A1 (Supplementary material).

Fig. 5. Melt pool evolution based on Molecular Dynamics: (a) melt pool model; (b) SLM treatment; (c) LSMMP treatment.

Material flow evolution was analyzed from microscopic and macroscopic perspectives. Microscopically, forced acceleration of atoms inside the melt pool increases cooling rate. Liu et al. [27] used Mean Square Displacement (MSD) to study atomic motion:

$$\mathrm{MSD} = \frac{1}{N}\sum_{i=1}^{N}\left[\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(t)\right]^2$$

where **r**i(t) is atom i position at time t, N is atom number, and Δt is time step change. Fig. 6 shows MSD curves for both processes. The LSMMP MSD vector components (dx, dy, dz) are much larger than SLM values (Fig. 6(a)). Atoms oscillate and spread after stress application, showing an obvious MSD jump and linear time relationship at the initial pulsed laser stage (Fig. 6(b)), indicating particularly strong atomic mobility. As temperature decreases, atoms arrange regularly, with MSD curves becoming horizontal at solidification temperature, forming regular arrangements with slight equilibrium position oscillations. Additional MSD results for different shock cases appear in Fig. A2 (Supplementary material), demonstrating violent convection inside the LSMMP liquid pool.

Fig. 6. The MSD of atoms in the melt pool: (a) squared dx, dy, dz directional displacements; (b) total squared displacement.

Macroscopically, laser shock-generated forces drive and accelerate melt pool flow, contributing to increased cooling rate. Internal melt pool behavior was simulated as shown in Fig. 7. CW laser input creates non-uniform temperature fields, producing an asymmetrical convection ring inside the plump liquid melt pool that surges from both sides to the surface, forming typical Marangoni convection. Khairrallah et al. [28] demonstrated the significant effects of recoil pressure and Marangoni convection in laser powder bed fusion. However, since the heat source remains on the top surface, the lower region is not directly influenced, maintaining high thermal stress. This issue is partially resolved by pulsed laser assistance. Fig. 7(b) shows top region depression from applied force, transforming the original symmetrical convective ring into multiple loops at top and bottom regions that accelerate flow and promote rapid heat transport.

Fig. 7. Computed temperature and vectors distribution under different processes: (a) SLM treatment; (b) LSMMP treatment.

While accelerated atomic motion and multiple convection mechanisms suggest affected cooling rates, the relationship between cooling rate and position within the melt pool requires clarification. Gan et al. and Karayagiz et al. [29, 30] studied temperature gradient G, solidification velocity R, and cooling rate C (C = G $\cdot$ R) in LAM, which determine final grain size, with G/R ratio controlling grain growth type. These parameters were extracted as shown in Fig. 8 [Figure 8: see original paper], with melt pool schematics indicating representative G and R prediction locations. In both processes, maximum G occurs at the melt pool bottom (with low R), while minimum G appears at the top (with high R) (Fig. 8(a) and (b)). The key difference is that LSMMP increases both G and R at all positions. Fig. 8(c) shows average cooling rate C along the melt pool centerline: from bottom to top, values are 475.7, 207.7, 176.3, and 164.9 K/s for SLM versus 562.9, 412.5, 329.3, and 371.2 K/s for LSMMP—demonstrating increased cooling rates regardless of location. Fig. 8(d) shows G/R values along the centerline: from bottom to top, 578.9, 221.6, 98.0, and 38.2 for SLM versus 520.1, 225.8, 80.5, and 17.4 for LSMMP. The lower G/R values under LSMMP lead to different grain growth types at various melt pool locations.

Fig. 8. The predicted temperature gradient G and solidification velocity R along the melt pool centerline for two process sets: (a) SLM; (b) LSMMP. Melt pool schematics with blue lines show representative G and R prediction locations; (c) cooling rate (G $\cdot$ R); (d) G/R values under both treatments.

3.3. Microstructure Analysis

Microstructures under different treatments were characterized to verify simulation results, as shown in Figure 9 [Figure 9: see original paper]. The SLM-processed melt pool cross-section shows a non-equilibrium structure of columnar and equiaxed dendrites (Fig. 9(a)). The enlarged bottom boundary view reveals good bonding between HEA and substrate, indicating excellent tensile properties. Columnar dendrites grow upward perpendicular to substrate boundaries (Fig. 9(b)). Lin et al. [31] identified columnar dendrites as typical LAMed HEA features. During LAM, the laser irradiation center creates a high-temperature gradient G to the edge cooling zone, driving columnar dendrite growth along G from the melt pool bottom (Fig. 9(b)). Solid/liquid (S/L) interfaces promote directional solidification from inside-out and bottom-to-top. In the middle and upper regions, lower G values near the heat source cannot drive columnar dendrite epitaxial growth. EDS results (Fig. 9(c)) show uniform Cr, Fe, Co, and Ni distribution in columnar dendrites.

Fig. 9. Samples under SLM treatment: (a) melt pool section microstructure, (b) local SEM image of columnar crystals, (c) EDS result from (b); Samples under LSMMP treatment: (d) melt pool section microstructure, (e) local SEM image of equiaxed crystal, (f) EDS results at points A and B in (e).

In contrast, LSMMP treatment transforms growing columnar dendrites into equiaxed dendrites in the middle and top regions, producing a Columnar-Equiaxed Transition (CET). The liquid melt pool oscillates vertically and spreads laterally, forming multiple convective loops (Fig. 10(a)). The relationship between temperature gradient G and solidification velocity R is crucial (Fig. 10(b)). LSMMP reduces G/R values below those of SLM in middle and top regions, changing the recrystallization mode to equiaxed dendrite growth. Additionally, high cooling rates increase grain nucleation rates, favoring small equiaxed dendrite formation. In Fig. 9(f), each CoCrFeNi element accounts for approximately 25% (shaded area indicates reasonable distribution). Dendrite point A and interdendritic point B show equal Co and Ni content, slightly lower Cr, and marginally out-of-range Fe attributed to extensive HEA-substrate mixing. Reduced content of other elements also contributes to this result. Abolkassem et al. [32] reported Cr phase cluster and Cr2O3 formation, reducing Cr content during processing, while other elements likely form solid solutions with Fe. Figure 11 [Figure 11: see original paper] shows XRD patterns of CrFeCoNi powder and HEAs under different processes. Three typical FCC peaks—(111), (200), and (220)—dominate the 20-90° range, indicating stable FCC structures under all processing conditions. Co also forms BCC solid solutions with Fe, consistent with Abolkassem et al. [32].

Fig. 10. (a) Columnar-Equiaxed Transition (CET) in LSMMP treatment, (b) microstructure selection map for solidification morphology as a function of G and R [29].

Fig. 11. X-Ray Diffraction patterns of samples under different treatments.

3.4. Nano-indentation Analysis

Microstructural changes directly affect mechanical properties. Under identical experimental loading conditions, nanoindentation results show position-dependent displacements within the melt pool. In Fig. 12(a), (b), and (c), post-LSMMP displacements at top, middle, and bottom regions are 776 nm, 759 nm, and 624 nm, respectively—smaller than SLM values of 786 nm, 894 nm, and 682 nm. This indicates improved deformation resistance. LSMMP produces equiaxed dendrites while SLM yields columnar dendrites; under identical loads, equiaxed dendrites exhibit significantly stronger isotropic deformation resistance than columnar dendrites. At the melt pool bottom, the opposite trend occurs, with stronger deformation resistance than middle and top regions. Nano-hardness results (Fig. 12(d)) show LSMMP values of 3.09 GPa, 2.83 GPa, and 4.67 GPa for top, middle, and bottom regions, respectively—superior to SLM values of 2.54 GPa, 2.19 GPa, and 4.32 GPa. This confirms that CET under LSMMP provides beneficial mechanical property improvements.

Fig. 12. Nanoindentation load-displacement curves in different areas: (a) Top, (b) Middle, and (c) Bottom of melt pool; (d) Hardness in different areas.

4. Conclusions

A new LSMMP method utilizing LSP on liquid melt pools was investigated through combined numerical simulation and experimental studies to understand the laser shock-melt pool interaction mechanism. The process was systematically verified from three perspectives: process dynamics, microstructure evolution, and mechanical properties. The results demonstrate an effective in-situ modulative tool for controlling additive manufacturing, with key conclusions summarized as follows:

1. The convection mechanism of LSMMP melt pools is revealed. Pulsed laser-induced plasma acts on the melt pool, promoting flow mode transformation from Marangoni effect to multi-convective loops, successfully increasing cooling rate by accelerating melt pool flow.
2. The microstructure evolution law of CrFeCoNi HEAs is established. Pulsed laser action increases melt pool growth rate and induces CET transformation.
3. Non-destructive real-time fabrication of CrFeCoNi HEAs with stable FCC structures is achieved. Nano-hardness in top, middle, and bottom melt pool regions is improved without segregation defects.

CRediT Authorship Contribution Statement: Heng Lu: Investigation, Visualization, Integration, Writing-Original Draft. Xiaohan Zhang: Resources. Jian Liu: Resources. Shusen Zhao: Resources and Supervision. Xuechun Lin: Resources and Supervision. Hui Li: Resources and Supervision. Yaowu Hu: Conceptualization, Methodology, Supervision, Funding Acquisition.

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Appendix A. Supplementary Material: This document provides supplementary information to "Study on laser shocking of melt pool in Laser Additive

Manufacturing of FeCoCrNi High-Entropy Alloys."

1. Cooling Process

Molecular Dynamics (MD) simulation of LSMMP comprises five stages: relaxation, heating (2000 K), constant temperature annealing, shocking, and cooling. Before cooling, the shocking module is removed to observe liquid surface oscillation. Total cooling duration is 40 ps (Fig. A1); SLM process excludes the shock module. The liquid melt pool oscillates after stress application, with shock waves propagating three-dimensionally (Fig. A1(b)). At 4 ps, the oscillated melt pool diffuses into the solid phase and substrate. At 20 ps, melt pool temperature decreases and gradual solidification begins. Post-cooling, the SLM model shape shows no significant change, while the LSMMP model becomes flat rather than recovering to the SLM state. Melt pool profile changes agree with 3D profile data, indirectly indicating increased cooling rate in the shaken melt pool.

Fig. A1. The cooling process of melt pool based on Molecular Dynamics: (a) SLM treatment; (c) LSMMP treatment.

2. Different Shock Cases

Additional shock cases with impact velocities of 1.5, 2, and 2.5 km/s were simulated (Fig. A2(a)). Results show no additional benefits from larger shock waves —too small is ineffective, too large destroys the melt pool. Previous experiments using SLED = 93.59 J/cm2 produced beneficial oscillation, corresponding to the 1 km/s MD case. At this condition, melt pool atomic MSD is maximized, indicating particularly strong atomic movement that accelerates heat source escape. Other MSD curves are lower than the 1 km/s case. Three-component MSD vectors (dx, dy, dz) are also displayed in Fig. A2.

Fig. A2. The MSD of atoms in the melt pool: (a) total squared displacement under different shock conditions; squared dx, dy, dz directional displacements: (b) 1.5 km/s, (c) 2 km/s, and (d) 2.5 km/s.

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