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Abstract

With growing interest in Laser Additive Manufacturing (LAM) of High-entropy alloys (HEAs) during most recent years, the design of compositional elements and process strategies are primary methods to overcome undesirable microstructures and defects. Here we propose a new approach, a novel real-time Laser Shocking of Melt Pool (LSMP), to obtain melt pool modifications for yielding HEAs with desired characteristics. LSMP 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 LSMP 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 LSMP 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

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

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Abstract

In recent years, growing interest in laser additive manufacturing (LAM) of high-entropy alloys (HEAs) has led to element design and scanning strategies being the primary methods for overcoming defects such as porosity and segregation. Here, we propose a novel approach—real-time Laser Shocking of Melt Pool (LSMP)—to modify the melt pool and produce superior HEAs. LSMP introduces a pulsed laser into a liquid melt pool created by a continuous-wave laser, enabling non-destructive, real-time fabrication of high-performance HEAs. Numerical simulation reveals the convection mechanism of the melt pool during LSMP, showing that pulsed laser intervention transforms the flow pattern from Marangoni-driven convection to multi-convective rings, which accelerates melt pool flow and significantly inhibits columnar crystal growth. Experimental results demonstrate the microstructural evolution during LSMP, where CrFeCoNi HEAs form a stable FCC structure without segregation or other defects. Meanwhile, the microstructure undergoes a Columnar-Equiaxed Transition (CET), yielding CrFeCoNi HEAs with enhanced nano-hardness. Furthermore, the reduction in (111) interplanar spacing demonstrates that laser shock induces beneficial compressive stress. Therefore, introducing laser shock under appropriate conditions is necessary for online melt pool control.

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

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1. Introduction

High-entropy alloys (HEAs), first introduced by Yeh et al. [1] as a revolutionary departure from conventional single-principal-element alloy design, exhibit exceptional properties that have attracted widespread attention across fundamental research and engineering manufacturing. However, typical metallurgical defects such as porosity and segregation in conventional as-cast HEAs limit their potential applications. Fortunately, Brif et al. [2] first demonstrated that laser additive manufacturing (LAM) could produce HEAs with superior mechanical properties compared to cast samples, establishing the feasibility of LAM-processed HEAs. This technology not only shortens the process cycle but also provides a faster, more efficient method for manufacturing complex HEA components. Moghaddam et al. [3] have also presented a comprehensive review of the current state and future prospects of additive manufacturing for HEAs.

Among various HEA systems, FeCoCrNi-based alloys processed by laser additive manufacturing have been the most extensively studied. Zhou et al. [4] fabricated carbon-containing $FeCoCrNiC_{0 \cdot 05}$ HEAs by selective laser melting (SLM), achieving a single face-centered cubic (FCC) structure without carbide phases and uniform carbon distribution under optimal parameters. Zhu et al. [5] prepared CoCrFeNiMn HEAs by SLM with uniform elemental distribution, though slight Mn segregation occurred at melt pool boundaries. Peyrouzet et al. [6] obtained $Al_{0 \cdot 3}CoCrFeNi$ HEAs via SLM with tensile strength up to 896 MPa and yield strength of 730 MPa, also exhibiting a single FCC structure. Clearly, as noted by Li et al. [7], research focus has increasingly shifted toward material performance.

However, the high thermal stress induced by melt pool thermal cycling during LAM poses significant challenges. Zhang et al. [8] observed cracks in CoCrFeNiMn HEA samples under different scanning strategies, resulting in low densities, a finding also reported by Niu et al. [9]. Many researchers have sought solutions to this problem. For instance, Jiang et al. [10] showed that adding Fe-based amorphous material significantly reduces internal stress through the presence of an FCC phase. Additionally, the uncertain cooling rate of the melt pool—a critical factor—directly affects recrystallization behavior, leading to HEAs with varying properties. Li et al. [11] revealed the formation mechanism of microstructures in rapidly cooled HEAs through molecular dynamics (MD) simulation. Currently, most HEAs prepared by laser melting deposition (LMD) exhibit typical dendritic structures because the LMD scan rate is significantly lower than that of SLM, resulting in low cooling rates that prevent equiaxed crystal formation. Tong et al. [12] found that LAM-produced CoCrFeNiMn HEAs consist primarily of columnar crystals inside the melt pool, while equiaxed grains form outside the melt pool; after heat treatment at 1100 °C, the structure becomes completely equiaxed. However, subsequent heat treatments, such as those employed by Knowles et al. [13] after direct metal laser sintering (DMLS) or hot isostatic pressing (HIP) applied by Li et al. [7] after SLM, compromise process continuity and production efficiency. Nevertheless, Tong et al. [14] demonstrated that varying process parameters such as laser power and scanning speed can directly produce different microstructures, as the ratio of thermal gradient to solidification rate within the melt pool dominates the Columnar-Equiaxed Transition (CET).

Therefore, online regulation of the melt pool during LAM is particularly important. Laser Shock Peening (LSP) is an advanced technology that not only induces high compressive stress on metal surfaces but also enables micro-nano level control. For example, Hu et al. [15, 16] realized ultrafast direct fabrication of plasmonic nanoarrays using LSP. We propose a novel synchronous Laser Shocking of Melt Pool (LSMP) method to suppress thermal stress, enhance melt pool convection, and inhibit columnar crystal growth. This extends the work of Tong et al. [14], who used LSP as a post-processing treatment, to achieve in-situ modification for improving LAM-processed HEAs. Although pulsed lasers are widely used for property enhancement, to our knowledge, no research has investigated synchronous hybrid additive manufacturing with laser shocking of the melt pool to overcome liquid metal surface tension. In this paper, we study the LSMP mechanism through combined experiments and numerical simulations, revealing the convection mechanism within the melt pool under pulsed laser assistance. Consequently, we obtain the microstructural evolution law for HEAs produced by LSMP, achieving non-destructive, real-time production of higher-performance CoCrFeNi HEAs.

2.1. Materials and Experiment

The LSMP method introduces a pulsed laser into a liquid high-entropy alloy melt pool produced by a continuous-wave (CW) laser, as shown in Fig. 1(a). The substrate consisted of 45 steel measuring 30 mm × 30 mm × 1 mm, which was polished and cleaned with ethanol to ensure surface cleanliness. The experimental material was equiatomic CrFeCoNi powder prepared by vacuum atomization, with particle sizes ranging from 15 to 45 m, exhibiting good fluidity and sphericity. The powder morphology and composition analysis are shown in Fig. 1(b) and (c), respectively. The powder layer thickness was 1 mm. The experimental equipment included a 1 kW continuous-wave fiber laser (Shenzhen Chuangxin Laser Co., Ltd.) and a pulsed laser. The selective laser melting (SLM) process was conducted in a high-purity argon atmosphere with a gas flow rate of 3 L/min. The process parameters were: laser power 800 W, platform moving speed 1000 r/min, and spot diameter 3 mm. The pulsed laser parameters were: laser energy 3 J, pulse width 10 ns, repetition frequency 10 Hz, and spot diameter 1 mm. The CW laser beam was perpendicular to the substrate, while the pulsed laser beam was inclined at -10° from the vertical.

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

2.2. Test Methods

Samples were characterized from three perspectives: process monitoring, microstructure and phase composition, and mechanical properties. First, a Chronos 1.4 high-speed camera (Kron Technologies, Canada) monitored the manufacturing process, while a NewView™ 9000 Series white-light interferometric 3D profiler (ZYGO, United States) measured sample topography. Second, cross-sections were prepared by sectioning along the normal direction, followed by polishing and cleaning, then etching 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 a MIRA3 scanning electron microscope (SEM) (Tescan, Czech Republic). To determine the phase composition of the original CoCrFeNi powder and processed samples, a D8 ADVANCE X-ray diffractometer (XRD) (Bruker, Germany) was employed, using copper target material, a scanning range of 20–90°, and a scanning speed of 5°/min. Finally, mechanical properties were evaluated using an iNano nanoindenter (KLA-Tencor, United States) with a 50 mN load, testing the upper, middle, and bottom regions of the cross-section.

2.3. Calculation

Molecular dynamics (MD) simulation: An iron sphere with a radius of 15 Å was assigned an initial velocity (V_0) for the LSMP process based on the following equations [17, 18]:

$$V_0 = \sqrt{\frac{2P}{m\tau}}$$

where I_0 is the nominal laser intensity, τ is the pulse duration, m is the mass of the iron sphere, P is the pressure generated during laser irradiation, and α is a factor accounting for the increase in plasma thermal energy from laser absorption. A typical velocity of 1 km/s was applied, yielding a peak pressure of 0.33 GPa based on Eq. (10) for the present conditions. The CoCrFeNi HEA and 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) in C style was employed for calculations, using the potential function for HEAs developed by Mi et al. [19]. The NVT ensemble was applied, heating the system to 2000 K with a time step of 0.001 ps.

Finite element modeling: A three-dimensional numerical model of laser-melt pool interaction was established based on finite element principles to predict the temperature field during SLM. To maintain computational efficiency without compromising accuracy, the following assumptions were made: (1) plasma and metal vapor behave as ideal gases; (2) shielding gas effects on the process are negligible; (3) computational fluids are laminar, Newtonian, and incompressible.

Conservation equations: Fluid flow and heat transfer in the LAM process are governed by mass, momentum, and energy conservation equations [20, 21]:

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 gravitational acceleration, T is temperature, h is material enthalpy, and k is thermal conductivity.

Laser heat source: A Gaussian volume heat source model was employed [22]:

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

where Q is laser power, H is the height of the laser heat source, α bs is material absorptivity, and R_0 is the effective laser beam radius. Theoretically, over 95% of the total laser energy is concentrated within the radius R_0.

Driving forces: Recoil pressure was modeled using a widely accepted expression [23]:

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

where P_0 is atmospheric pressure, R is the universal gas constant, ΔH is vaporization enthalpy, T is liquid-gas equilibrium temperature at a given pressure, ΔV is the difference between specific volumes of liquid and gas, and V is the specific volume of gas. Surface tension was expressed as a temperature-dependent function [20]:

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

The Marangoni force on the fluid surface is given by [20]:

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

where T is liquid surface temperature, T_0 is reference temperature, γ_0 is surface tension at T_0, and the negative sign indicates the force direction opposes the surface tension gradient.

Pulse pressure: Pulse pressure is generated by accelerating impact on the melt pool surface in the vertical direction. Based on theoretical analysis and experimental verification, the pulse pressure formula is [24]:

$$P_{\max} = 0.0123\alpha Z^{0.5} I_0^{0.5} \quad \text{(GPa)}$$

where P is pulse pressure, α is interaction efficiency, Z is reduced shock impedance, and I_0 is laser power density.

Geometric model and boundary conditions: As shown in Fig. 2, the computational domain measured 30 mm × 7 mm × 10 mm with a grid resolution of 0.15 mm. A 5 mm fluid region represented the HEA powder, while a 5 mm void region represented the atmospheric environment for observing the free surface. Energy and pressure boundary balance conditions were applied at all boundaries. Implicit SOR and VOF algorithms were used to capture and update free surfaces through user-defined functions, with boundary conditions imposed on all mesh elements until calculation completion.

Fig. 2. Schematic diagram of computational domain.

3.1. Surface Topography

To explore LSMP evolution, real-time melt pool images were captured for both processes, as shown in Fig. 3 and Video 1 (Supplementary Material). Fig. 3(a) records the real-time melt pool behavior during SLM, where CW laser input fully melts the CoCrFeNi powder, gradually forming a plump melt pool ahead of the solidification zone. In contrast, the LSMP process exhibits distinct characteristics. Fig. 3(b) shows plasma clusters induced by the pulsed laser, with the most significant effect being the shock wave-driven alteration of melt pool convection. During the 3.87 ms transient process, the melt pool surface area expands after each laser shock, facilitating heat escape and increasing cooling rate. Subsequently, surface tension restores the melt pool to its original state before the next pulse. Throughout the manufacturing process, the melt pool cools more rapidly. 3D profile data confirmed these observations. CW laser input fully melts the CoCrFeNi powder, producing an arc-shaped melt pool as shown in Fig. 4(b), which hinders rapid heat dissipation. In contrast, Fig. 4(c) reveals that LSMP changes the melt pool profile, making it wider and flatter. The melt pool height decreases while the bottom width increases, yet this does not compromise the forming process. Instead, it indirectly indicates that the shaken melt pool solidifies before returning to its original arc shape, demonstrating increased cooling rate. This phenomenon breaks the conventional cooling pattern where the heat source remains centered in the chill layer during LAM.

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

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

3.2. Evolution of Cooling Rate

Melt pool morphology changes are attributed to cooling rate variations. A CoCrFeNi HEA model was established for MD simulation, as shown in Fig. 5(a). Fig. 5(c) demonstrates that the liquid melt pool oscillates under applied stress, with obvious deformation at the top spreading outward. The shock wave propagates three-dimensionally, and the melt pool quickly recovers. Similar results show that after cooling, the LSMP melt pool size differs from the SLM model, becoming wider and flatter. These profile changes agree with the 3D profile data. Additional cooling process details at different time steps are provided in Fig. A1 (Supplementary Material).

Fig. 5. Melt pool evolution based on molecular dynamics: (a) melt pool model; (b) SLM treatment; (c) LSMP treatment.

The cooling rate evolution involves two mechanisms. Microscopically, atoms within the melt pool accelerate under applied force, increasing cooling rate. Liu et al. [25] commonly 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** (t) is the position of atom i at time t, N is the number of atoms, and Δt is the time step change. Fig. 6 shows MSD curves for atoms in the melt pool region under both processes. The MSD components in dx, dy, and dz directions for LSMP are much larger than for SLM (Fig. 6(a)), indicating that stressed atoms oscillate and spread outward. Additionally, MSD exhibits a distinct jump and linear time dependence when the pulsed laser acts on the melt pool (Fig. 6(b)), demonstrating exceptionally strong atomic mobility that accelerates heat dissipation. As temperature decreases, atoms begin arranging regularly. Upon reaching solidification temperature, MSD curves plateau as atoms form ordered arrangements with only slight equilibrium position relaxation. Additional MSD results for different shock cases are shown in Fig. A2 (Supplementary Material).

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

Macroscopically, melt pool flow is driven and accelerated, providing another mechanism for increased cooling rate. An internal melt pool model was constructed to understand this behavior, as shown in Fig. 7. CW laser energy input creates a downward force along the vertical centerline, generating a symmetric convection ring inside the plump liquid melt pool that surges from both sides to the surface, forming the typical Marangoni effect. Khairrallah et al. [26] demonstrated the significant influence of recoil pressure and Marangoni convection in laser powder bed fusion (L-PBF). However, the heat source remains trapped in the middle and lower regions (Fig. 7(a)), explaining persistent high thermal stress. Fortunately, pulsed laser assistance solves this problem. Fig. 7(b) shows a depression in the top region from applied force, altering the original symmetric convection ring and forming multiple convective loops in the top and bottom regions. This accelerates flow and promotes rapid heat source movement and dissipation.

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

The temperature-time relationship extracted from the internal melt pool model is shown in Fig. 8. Distinct temperature profiles appear under the two processes. The cooling rate C = ΔT/s^{-1} per unit time was calculated, where ΔT is temperature change and s^{-1} is 1 second. After reaching the peak temperature, LSMP solidifies rapidly with a cooling rate of -4.84 $\times$ 10^2 K/s, superior to SLM. Thus, LSMP effectively increases cooling rate.

Fig. 8. Computed temperature-time curve for melt pool.

3.3. Microstructure Analysis

Based on LAM' s layer-by-layer manufacturing principle, CoCrFeNi powder undergoes remelting and solidification during heating, causing structural changes where grain growth morphology is closely related to cooling rate. Under SLM, the melt pool cross-section shows a non-equilibrium structure comprising columnar and equiaxed dendrites (Fig. 9(a)). The enlarged view of the bottom boundary reveals good bonding between the HEA and substrate, indicating excellent tensile properties. Columnar dendrites at the melt pool bottom grow upward perpendicular to the substrate boundaries. During LAM, the laser irradiation area serves as the heat source center while the processed area acts as the chill layer, creating a high-temperature gradient that drives columnar dendrite growth upward along the gradient (Fig. 9(b)). Solidification proceeds directionally from inside to outside and bottom to top. In the middle and upper melt pool regions, the lower temperature gradient cannot drive epitaxial columnar growth. EDS results for the columnar dendrite region in Fig. 9(b) show uniform distribution of Cr, Fe, Co, and Ni elements (Fig. 9(c)) without segregation defects. Lin et al. [27] also identified columnar dendrites as a typical feature of LAM-processed HEAs.

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

Figs. 9(d) and (e) reveal that the LSMP melt pool exhibits an equilibrium structure composed of equiaxed dendrites, demonstrating a clear Columnar-Equiaxed Transition (CET). Hunt [28] proposed a model where complete equiaxed dendrite growth occurs when the equiaxed grain volume fraction $\Phi > 0.49$, while completely columnar structures correspond to $\Phi < 0.0066$. Gaumann et al. [29] proposed a revised model:

$$\Phi = \frac{4}{3}\pi N_0 \left(\frac{a}{GV}\right)^n \left[\frac{1}{\ln\left(\frac{1}{\Phi}\right)}\right]^{n-1}$$

where G is temperature gradient, V is solidification rate, $N_0 = 2 \times 10^{15}$ m^{-3} is nucleation number, Φ is equiaxed grain volume fraction, and a and n are material constants (n = 3.4, a = 1.25 $\times$ 10^6 K$^{3\cdot4}$/m$\cdot$s). Setting Φ to the lower critical value $\Phi c = 0.0066$, Gan et al. [30] derived a criterion based on the G^n/V ratio for completely columnar dendrites:

$$\frac{G^n}{V} > K \quad \text{where} \quad K = 2.7 \times 10^{24}\,\mathrm{K}^{3.4}/\mathrm{m}^{4.4}\mathrm{s}$$

This microstructure relationship between solidification speed and temperature gradient is crucial (Fig. 10(a)). Clearly, LSMP alters the directional solidification mode under the same G condition. Fig. 10(b) shows the liquid melt pool oscillating vertically and spreading outward, forming multiple convective loops. Combined with increased surface area and cooling rate (Fig. 8), this directly accelerates solidification rate V, increasing nucleation rate while decreasing growth rate. Consequently, $G^n/V < K$ occurs during LSMP, transforming the recrystallization mode to complete equiaxed dendrite growth. In Fig. 9(f), dendrite point A and interdendritic point B show equal elemental compositions of Cr, Fe, Co, and Ni. Abolkassem et al. [31] showed that Cr phase clusters and Cr_2O_3 formation reduce Cr content, while other elements form solid solutions with Fe, resulting in higher Fe composition.

Fig. 10. (a) Microstructure selection map for solidification morphology as a function of G and V [29]; (b) Columnar-Equiaxed Transition (CET) occurring during LSMP treatment.

3.4. Phase Composition

Figure 11 shows XRD patterns for CrFeCoNi powder and processed HEAs. Three typical FCC peaks—(111), (200), and (220)—dominate the 20-90° range, confirming stable FCC structures under all processing conditions. Ni and Cr also form BCC solid solutions with Fe, consistent with Abolkassem et al. [31]. Under LSMP, the (111) peak shifts slightly to higher angles (Fig. 11(a)) due to reduced interplanar spacing. In the orthorhombic system, interplanar spacing d is determined by Miller indices (h k l) through:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

For the cubic system where a = b = c, this simplifies to:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Peak fitting yielded lattice constants of 3.55 Å and 2.87 Å for the two conditions, corresponding to (111) interplanar spacings of 2.05 Å and 1.66 Å, respectively (Fig. 11(b). At the macroscopic stress level across multiple crystal scales, LSMP-induced compressive stress reduces interplanar spacing, causing the XRD peak shift to higher angles. González et al. [32] showed that residual compressive stress can effectively inhibit hot crack propagation, which is beneficial.

Fig. 11. (a) X-ray diffraction patterns and (b) interplanar spacing and lattice constants of samples under different treatments.

3.5. Nano-Indentation Analysis

Microstructural changes directly affect mechanical properties. Under identical loading conditions, nanoindentation results show different displacements at various melt pool positions. In Figs. 12(a) and (b), displacements in the upper and middle regions after LSMP treatment are 879 nm and 909 nm, respectively, superior to SLM results, indicating improved deformation resistance. These regions lie within the strong influence zone of the laser shock wave, where LSMP produces equiaxed dendrites compared to SLM' s columnar dendrites. Under the same load, equiaxed dendrites exhibit significantly stronger isotropic deformation resistance than columnar dendrites. At the melt pool bottom, the opposite trend occurs due to greater distance from the shock wave (Fig. 12(c)). While columnar dendrites tightly bonded to the substrate show better composite tensile strength under indentation, nano-hardness results demonstrate that LSMP-treated samples achieve 3.09 GPa, 2.83 GPa, and 4.67 GPa in the upper, middle, and bottom regions, respectively (Fig. 12(d)), all superior to SLM values. This confirms that CET under LSMP provides beneficial property improvements.

Fig. 12. Nanoindentation load-displacement curves in different regions: (a) top, (b) middle, and (c) bottom of melt pool; (d) hardness values in different regions.

4. Conclusions

In LAM of high-entropy alloys, online melt pool regulation is crucial. This study investigated a novel LSMP method that extends laser shock peening from solid surfaces to liquid melt pools. Combined with numerical simulation to understand the laser shock-melt pool interaction mechanism, the new process was systematically validated from three perspectives: forming process, microstructure, and mechanical properties. The results demonstrate the necessity of introducing laser shock, with key conclusions summarized as follows:

1. **Revealing the melt pool convection mechanism:** Plasma induced by the pulsed laser promotes transformation of melt pool flow from Marangoni convection to multi-convective loops, successfully increasing cooling rate by accelerating melt pool flow.
2. **Obtaining the microstructural evolution law for CrFeCoNi HEAs:** After pulsed laser action, the melt pool solidification rate increases, inducing CET transformation. Macroscopically, nano-hardness

in the top, middle, and bottom regions improves, without segregation defects.

3. **Achieving non-destructive, real-time fabrication of CrFeCoNi HEAs with stable FCC structures:** The reduction in (111) interplanar spacing proves that laser shock introduces beneficial compressive stress.

CRediT Authorship Contribution Statement

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

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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

The molecular dynamics (MD) simulation of Laser Shocking of Melt Pool (LSMP) proceeds through five stages: relaxation, heating (to 2000 K), constant temperature, shocking, and cooling. Before entering the cooling stage, the shocking module is removed to observe liquid surface oscillation. The total cooling duration is 40 ps, as shown in Fig. A1; the SLM process lacks the shock module. Clearly, the liquid melt pool oscillates after stress application, with shock waves propagating three-dimensionally (Fig. A1(b)). At 4 ps, the oscillating melt pool diffuses into both solid phase and substrate. By 20 ps, the melt pool temperature decreases and gradual solidification begins. After cooling, the SLM model shape shows no significant change, whereas the LSMP model does not recover to a similar state but becomes flat. These melt pool profile changes agree with 3D profile data, indirectly indicating that the shaken melt pool’ s increased cooling rate causes solidification before returning to the SLM-like state.

Fig. A1. Cooling process of melt pool based on molecular dynamics: (a) SLM treatment; (c) LSMP treatment.

2. Different Shock Cases

Additional shock cases with velocities of 1.5, 2, and 2.5 km/s were simulated, as shown in Fig. A2(a). Results indicate that larger shock waves do not provide additional benefits—too small is ineffective, while too large destroys the melt pool. Our previous experiments showed that 3 J laser energy produces beneficial oscillations, corresponding to the 1 km/s case in MD. At this condition, MSD of melt pool atoms is maximized, indicating particularly strong atomic movement that accelerates heat source escape. Other MSD curves are significantly lower. MSD components in dx, dy, and dz directions are also displayed for 1.5 km/s (Fig. A2(b)), 2 km/s (Fig. A2(c)), and 2.5 km/s (Fig. A2(d)).

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

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