

Article

Influence of Laser Direct Energy Deposition Process Parameters on the Structure and Phase Composition of a High-Entropy Alloy FeCoNiCrMn

Ekaterina Kovalenko , Igor Krasanov, Ekaterina Valdaytseva, Olga Klimova-Korsmik  and Marina Gushchina World-Class Research Center “Advanced Digital Technologies”, State Marine Technical University,
190121 Saint-Petersburg, Russia

* Correspondence: kovalenko.ek@inbox.ru

Abstract: High-entropy alloys are a unique class of alloys with high strength and hardness, good enduring quality and corrosion resistance, as well as other attractive mechanical properties for both scientific research and practical applications. Using these unique alloys together with the dynamically developing technology of laser direct energy deposition (L-DED) carries the prospects of obtaining large-sized complex-profile products with specified increased mechanical properties. The study of the influence of L-DED parameters on the formation of high-entropy alloys will expand knowledge about the influence of temperature and cooling rate on the formation of the structure, on the mechanical characteristics of high-entropy alloys and the formation of defects and use them for thermal processes involving high-entropy alloys. Preliminary modeling will predict the phase composition of alloys in conditions of high heating and cooling rates. In the work, optimal parameters were selected for obtaining high-entropy alloys based on FeCoNiCrMn by L-DED technology. It was also shown that FeCoNiCrMn alloys were divided into areas with a high content of elements (Fe, Co, Cr) and (Mn, Ni, Cu).



Citation: Kovalenko, E.; Krasanov, I.; Valdaytseva, E.; Klimova-Korsmik, O.; Gushchina, M. Influence of Laser Direct Energy Deposition Process Parameters on the Structure and Phase Composition of a High-Entropy Alloy FeCoNiCrMn. *Metals* **2023**, *13*, 534. <https://doi.org/10.3390/met13030534>

Academic Editor: Pavel Krakhmalev

Received: 4 February 2023

Revised: 1 March 2023

Accepted: 4 March 2023

Published: 7 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: high-entropy alloy; laser direct energy deposition; phase composition

1. Introduction

Because of the active development of modern mechanical engineering and manufacturing industry, there was a need to improve the performance characteristics of existing alloys. Promising materials are high-entropy alloys (HEA) with increased values of mechanical characteristics. Despite the high interest in HEAs at the moment, their industrial use is limited [1–5].

High-entropy alloys are a type of solid-soluble alloys consisting of several basic elements with the same or similar atomic ratio, where the atomic concentration of each element is approximately from 5% to 35% [6,7]. The term “high-entropy” indicates a high configuration entropy in an alloy, which is created by the random colonization of lattice sites by several species at significant concentrations on one solid solution lattice. It was assumed that this entropic contribution stabilizes a single-phase solid solution, redefining the enthalpy contribution in favor of competing phases and mixtures of phases. However, the effect of high entropy is much weaker than originally thought. The contribution of the configuration entropy does not outweigh the competing contributions of the enthalpy of lattice deformation, enthalpy of chemical mixing or mismatch of structural components, all of which contribute to the formation of competing phases, in particular intermetallics. As a result, many materials with the structure of a single-phase solid solution are unstable [8]. In the work [9], alloy CoCrFeMnNi after annealing in the temperature range from 750 °C to 900 °C, the peaks of the σ -phase with the main peak FCC are observed. When the annealing temperature rises above 850 °C, only FCC peaks are observed. In the work [10], was found that the evolution of the Fe₄₀Mn₄₀Co₁₀Cr₁₀ alloy nanostructure is controlled,

among other things, by modifying stacking fault energy and Gibbs free energy for the FCC-HCP phase transformation by allowing Mo or C. The addition of Mo reduced the change in Gibbs free energy, which resulted in increased metastability at 77 K. Adding C led to the opposite situation. It is also noted that the proportion of the hcp phase in $\text{Fe}_{40}\text{Mn}_{40}\text{Co}_{10}\text{Cr}_{10}$ continuously increased with an increase in the strain to 20%. With an increase in deformation above 20%, the intensity of the peak corresponding to the FCC face began to decrease, while the intensity of the HCP peak increased slightly. In turn, the structure of the solid solution, BCC, FCC or mixed structure, affects the mechanical properties of HEA [11].

The phase of the material is closely related to the properties. In addition, some HEA undergo phase transformation under certain conditions, and the mechanisms of phase transformation have not yet formed a system. Currently, the main factors affecting the microstructure of HEAs are, among other things, elements and temperature. The presence of a certain structure in the alloy depends on the type and percentage of certain elements in the alloy. For example, the large radius of the Al atom in the $\text{Al}_x\text{CoCrFeNi}$ alloy with an increase in the concentration of aluminum increases the distortion energy of the lattice and makes the FCC unstable, since the stacking density of the BCC (68%) is lower than that of the FCC and the HCP (74%), which facilitates adaptation to larger atoms and leads to a phase transformation between FCC, FCC + BCC and BCC [12–15]. Temperature also affects the phase transformation of HEA. The solid solution formed after alloying is in a metastable state, and the internal stress is removed during high-temperature sintering or heat treatment, and the metastable structure turns into a stable one [16].

Despite many features of the metastability of the HEAs, there are still some difficult tasks, such as the influence of various heat treatments. In addition, the cooling rate can play a crucial role in the microstructure's development and in the properties of high-entropy alloys [17–20]. Compared to traditional materials, the design and preparation of multicomponent materials are more complex. Since the discovery of new materials is a time-consuming and inefficient process, the trial-and-error method remains the main approach [21].

Laser direct energy deposition technology (L-DED) shows excellent superiority in fabricating structural and functional materials to conventional processing methods, such as casting, forging and welding. Metallic powders go through sufficient melting and solidification during the L-DED processes, leading to near-fully dense parts with excellent properties [22]. The interaction of laser radiation with materials is accompanied by high heating and cooling rates, which can be considered as nonequilibrium processing [23–25]. In this regard, it is expected that the formation of the structure will be largely determined by the diffusion-free flow of the formation of the phase composition. For example, in [26] was considered $\text{TiC}/\text{CoCrFeNi}$ with an FCC structure, which was cooled by two methods: in a furnace and a copper crucible, which affects the cooling rate of the samples. The samples had different microstructures, with an increased cooling rate, which was provided by cooling in a copper crucible, the microhardness was 1–15% higher. In [27], the HEA $\text{Co}_{22}\text{Cr}_{18}\text{Cu}_{20}\text{Mn}_{16}\text{Ti}_{24}$ with an FCC structure was considered. At cooling speeds less than 100 degrees for a second, a structure with small dendrites was isolated from the liquid. After that, hexagonal dendrites and an inter-dendritic region appeared. At a cooling rate of over 100 deg/s, small dendrites were not formed, these structures were skipped. In [17], NiCoFeCrGa with a mixed BCC and FCC structure was considered at cooling rates of 100–100,000 deg/s. As the speed decreased, the microhardness increased. There are also different concentrations of elements in BCC and FCC at different cooling rates. The results confirming the grouping of Co, Fe and Cr in the FCC phase and Ni and Ga in the BCC phase were obtained.

It is known that laser additive technology, in addition to numerous advantages, also causes defects. The absorption of the laser beam depends, among other things, on the type of material, size distribution and morphology of the powder particles in the HEA. Since HEAs consist of several components in different proportions with variable size

distribution, morphology and melting temperature, the heat distribution at the deposition mode fluctuates, resulting in a complex thermal gradient with non-uniform melt pool morphology and corresponding defects generation creating the need to optimize process parameters and improve the overall quality and properties of additive manufacturing products [28,29]. Porosity is critical for additive manufacturing parts as it greatly reduces their mechanical properties and performance. Usually inside the deposited parts there are pores of various sizes and profiles. Crack formation and residual stresses are interrelated. In laser additive processes, residual stresses arise as a result of rapid heating and cooling phenomena, leading to a thermal gradient and cooling mechanisms, respectively. When the tensile stress exceeds the tensile strength, the part begins not to release excess stress inside the bulk part, which leads to a crack [30–36].

Alloy FeCoNiCrMn are actively studying, including in the field of additive technologies L-DED. Thus, in the work [35], samples built at a laser power of 1000–1400 W were obtained. The microstructures of the samples contain both columnar grains and equiaxed grains, their ratios depend on the laser power. The mechanical properties of 1400 W samples made by the L-DED method are better than those of samples made by casting. In the work [37], Al was added to the high-entropy alloy FeCoNiCrMn, samples were deposited with laser power at 1400 W. With an increase in the Al content, there is a transformation from FCC to FCC+BCC. In the work [38], the laser power was used 60–3000 W when deposited FeCoNiCrMn, however, the optimal laser power values were 600, 800 and 1000 W at a scanning speed of 800 mm/min. The microhardness of the samples was about 200 HV. In the work [39], FeCoNiCrMn was deposited with a laser power of 1200 W. The average porosity of the samples is 0.012 %.

In the work [38], FeCrCoMnNi was studied. The higher the laser power, the stronger the hardening of dendritic columnar grains was obtained, the average grain thickness increases. Thus, as the laser power increases, there is a significant increase in the columnar grains of the dendrite. In the work [40], studied the effect of the diameter of the laser spot on the CoCuFeMnNi alloy. With a decrease in the diameter of the melt spot, the bath becomes deeper, respectively, this means that more heat is transferred to the bath the stronger the hardening of dendritic columnar grains.

In all the works above, laser powers of the order of 800–1400 W were noted. For production on an industrial scale, it is necessary to increase the productivity of deposition, including by increasing the laser power and determining the effect on the laser power on obtaining defect-free products. It is worth noting that with L-DED technology, a change in the laser power with the remaining unchanged parameters directly means a change in the cooling rate: an increase in the laser power leads to a decrease in the cooling rate [41].

This work is aimed at studying the influence of the laser power and power density of laser radiation on HEA FeCoNiCrMn in order to select a deposition mode to increase productivity using of deposition high-entropy alloys using the L-DED technology. The influence of the cooling rate on the formation of the structure, phase composition and mechanical properties in the deposited FeCoNiCrMn will be considered. Preliminary modeling of the phase composition of the alloy will be carried out in order to determine the accuracy of the simulation.

2. Materials and Methods

To obtain samples of the HEA by L-DED technology, the powder FeCoNiCrMn was obtained by gas atomization technology. The powder fraction is 20–200 microns. The chemical composition of the powder in weight percentages was determined using a Tescan Mira3 scanning electron microscope (SEM) with the Aztec Live Advanced Ultim Max 65 energy dispersive microanalysis system point-by-point on a powder slice, the data of the spectrum labels were averaged for further modeling in Thermo-Calc (Table 1).

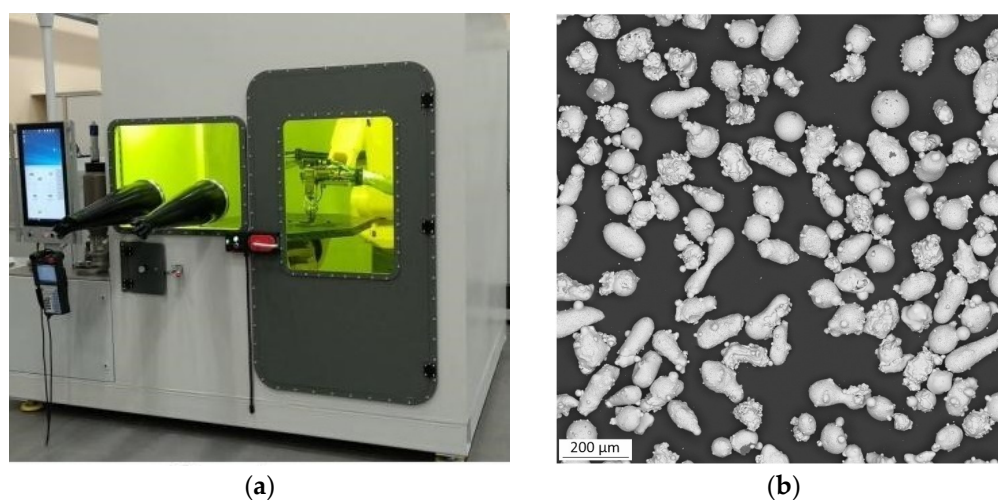
Table 1. Average chemical composition of FeCoNiCrMn powder.

Cr, %	Mn, %	Fe, %	Co, %	Ni, %	Cu, %
21.2	18.2	19	19.7	19.8	2.2

To obtain approximate theoretical results of the phase composition of the deposited samples from FeCoNiCrMn powder, the Thermo-Calc software package was used before deposition. For the calculation of L-DED processes, it is recommended to use the Scheil calculator in this software package [42]. The assumptions of local equilibrium, perfect liquid mixing, and no solid diffusion allows Scheil–Gulliver simulations to make time-independent predictions of the formation of solid phases from liquid using only the thermodynamic description of a system, given an algorithm that includes performing an equilibrium calculation at a current temperature, fixed pressure and composition of the system, separation of the liquid fraction into liquid and solid based on phase fractions from equilibrium calculation [43]. Thermo-Calc considers many thermokinetic parameters and has a database of experimental data, but does not consider the influence of parameters during deposition on the structure of samples. Despite this, with the help of Thermo-Calc, close to reality results are obtained for the calculation of the phase composition. When specifying the elements and their ratios in the alloy, the Thermo-Calc software package allows you to simulate the molar fraction of a solid, the presence of phases and the molar ratio of the elements of these phases depending on temperature.

Data from Table 1 were used for modeling. It is worth noting that carbon was detected in the powder section. Because of the carbon deposited on the surface of the chamber in the SEM, it is not possible to determine the amount of carbon in the sample using SEM, therefore, only a qualitative assessment was carried out. Carbon was not added to the powder composition during calculations in Thermo-Calc in order to avoid distortion.

A series of samples were built using an L-DED unit (ILIST-S) (Figure 1a). The complex includes industrial robot LRM-M20iB/25, fiber laser LS-3 Yb, head for laser deposition FLW D30, nozzle SO12, powder feeder. Figure 1b shows the FeCoNiCrMn powder, which was used for deposition of samples.

**Figure 1.** (a) 3D printer used for the current work; (b) FeCoNiCrMn powder.

Deposition was carried out in a sealed chamber in an argon atmosphere. For the study, eight samples were deposited in two series, the laser power, the diameter of the spot and the bead width changed in the series. In the first series, five samples were built: 1.8–2.6 kW. In the second series, three samples were built at lower values of laser power: 1.2–1.6 kW. The coefficient of the stability margin factor was equal to 10%. Scanning speed was equal 25 mm/s. Argon was used as a transporting gas. The layer height was 0.8 mm. The various parameters of deposition in two series by L-DED method and the sizes of samples are

presented in Table 2. Calculation of the laser power density has been added to the table. With a decrease in the laser power in the second series compared to the first, the values of the laser power density remained at the same level because of the decrease in the spot diameter. Further, the samples were examined for microhardness, phase and chemical composition of the samples.

Table 2. Laser direct energy deposition parameters (X-sample number).

Series	X	Laser Power, kW	Spot Size, mm	Bead Width, mm	Sample Size, mm	Power Density, W/mm ²
1.X	1	1.8	2.7	2.5	Height: 9 Width: 8	315
	2	2.0				350
	3	2.2				384
	4	2.4				419
	5	2.6				454
2.X	1	1.2	2.1	2	Height: 5.7 Width: 8	347
	2	1.4				404
	3	1.6				462

Sample preparation was performed using grinding sandpapers with step-by-step reduction of the grit size, from P180 to P1200. Polishing was performed on special polishing cloths using colloidal suspension with silicon oxide. Grinding was carried out for 3 min at sandpaper with a load of 25 N. Polishing was performed for 10 min with a load of 25 N. Microstructure studies were performed on a DMI 5000 optical microscope (Leica, Germany) using the “Axalit” program (Axalit, Russia). Structural and chemical analyses were performed on a Tescan Mira3 scanning electron microscope (TESCAN, Czech Republic) with “Oxford Aztec” software (Oxford Instruments NanoAnalysis, UK). X-ray diffraction (XRD) was performed using a Bruker D2 Phaser diffractometer with Cu K α radiation measured at 2 θ from 20° to 100°, operating at 30 kV and 10 mA with a 2 θ step size of 0.02 and exposure time of 0.1 s. Microhardness measurements were made using an FM-310 microhardness tester (Future Tech, Japan) at a load of 300 g. The indentations were applied over the entire height of the samples, starting from the substrate. 12 indentations were made and the distance between them was 650 μ m.

3. Results

3.1. Modeling

Figure 2 shows the calculation of phases for the FeCoNiCrMn alloy using the Sheil-Gulliver model [44], which allows us to consider the high cooling rates characteristic of our process of deposited products of HEAs. According to the calculation results, samples of this composition have a phase with a FCC structure. The separation of most (about 90%) of the solid phase from the liquid occurs up to 1200 °C in the form of an FCC solid solution. Figure 2 shows the elements that are present in the FCC phase, and the molar ratio of these elements in the phase during solidification. Cu and Mn elements at the beginning of solid phase separation fall out in a smaller molar percentage of the percentage composition of the powder and during cooling increase their concentrations in the alloy when they fall out into the phase: for the last remaining 10% of the liquid phase, Cu and Mn elements raise their concentrations in the solid phase by at least 5% each. Here we can note the elements Fe, Co, Cr, which at the beginning are released into the solid phase in a higher molar percentage than in the powder composition, while the molar content of elements of this group at the beginning of the precipitation of the FCC phase is quite close and amounts to Cr—22.76%; Fe—22.47%; Co—21.96%. And when cooling, the molar percentage of these elements only decreases. Next denote the groups of elements by the temperature of the beginning of crystallization of the elements: “Group A”—(Fe, Co, Cr), “Group B”—with a lower temperature of the beginning of crystallization, which includes elements (Mn, Ni, Cu).

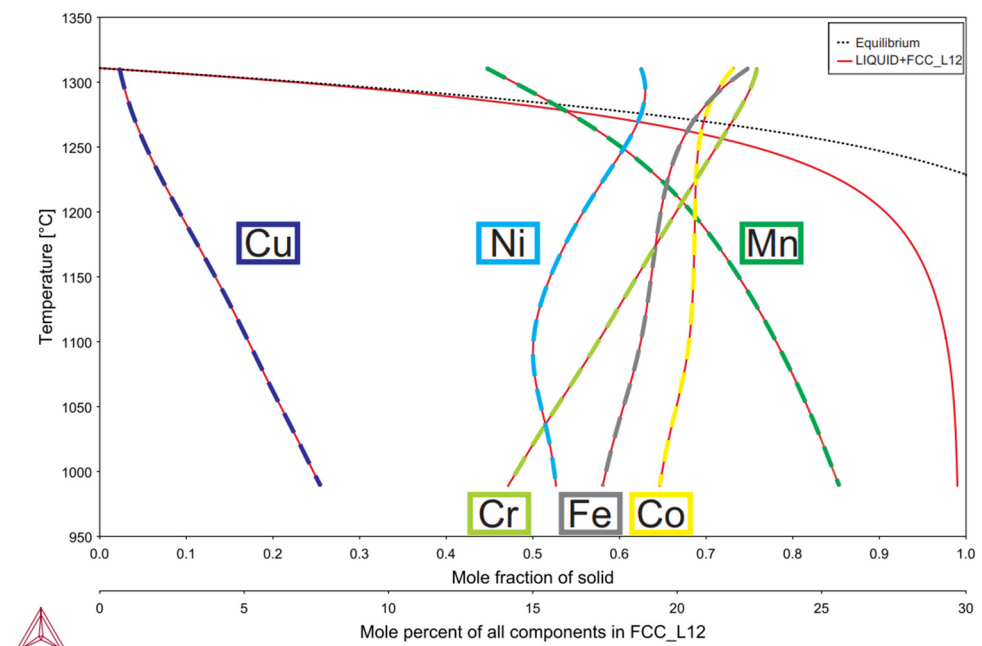


Figure 2. Solid phase precipitated from the liquid phase and molar ratio of the elements of the FeCoNiCrMn FCC phase during cooling.

The simulation results allowed us to predict that the most likely structure of solid solutions from FeCoNiCrMn powders will have an FCC lattice. The elements of group A were highlighted. In addition, the simulation showed that the formation of 80% of the solid phase from the liquid occurs in the range from 1312 °C to 1240 °C during cooling.

3.2. Microstructure and Chemical Composition of HEA

In samples No. 1.1 and No. 1.5, Figures 3 and 4 show the division of elements into areas with an increased content of elements of group A and group B. Next, denote “Area A”—an area with an increased content of elements of group A, similarly, denote “Area B”—an area with an increased content of elements of group B. SEM image on a Figure 3 shows us one single phase, which is colored in light-grey, and just a few pores. The same thing true for the Figures 4–7. In addition, in Figures 4 and 7 we can see cracks along with multiple number of pores.

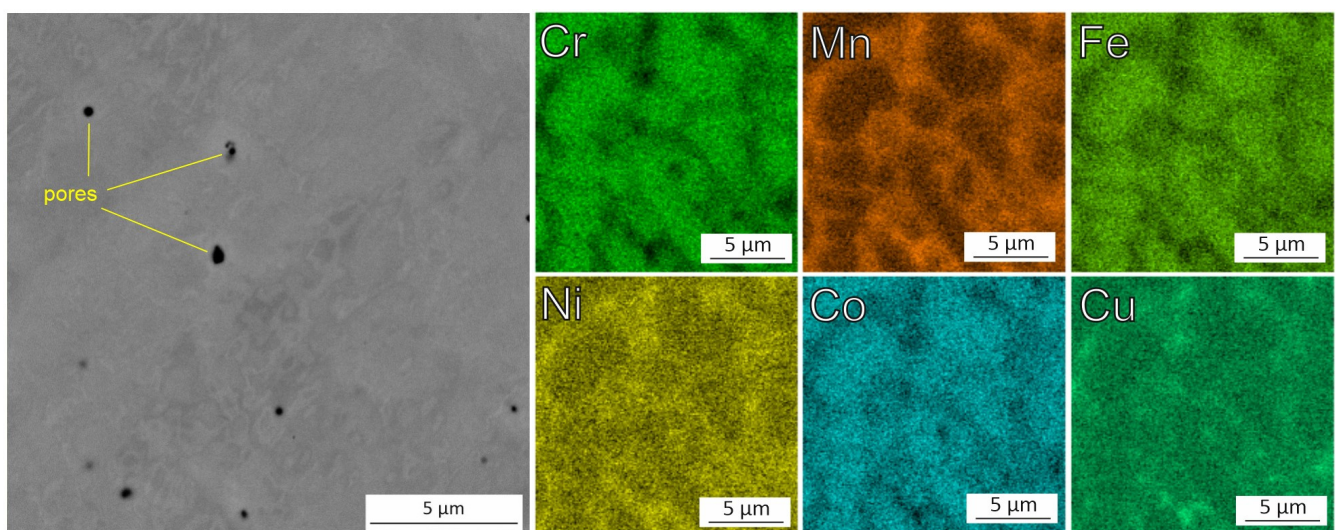


Figure 3. EDS analysis results for L-DED sample No. 1.1.

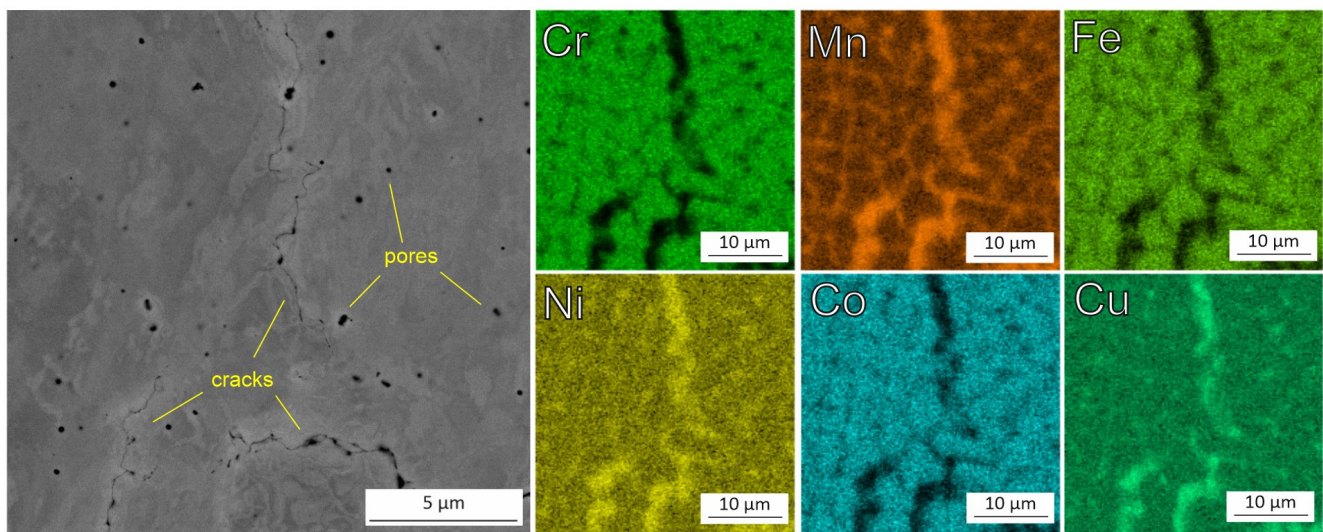


Figure 4. EDS analysis results for L-DED sample No. 1.5.

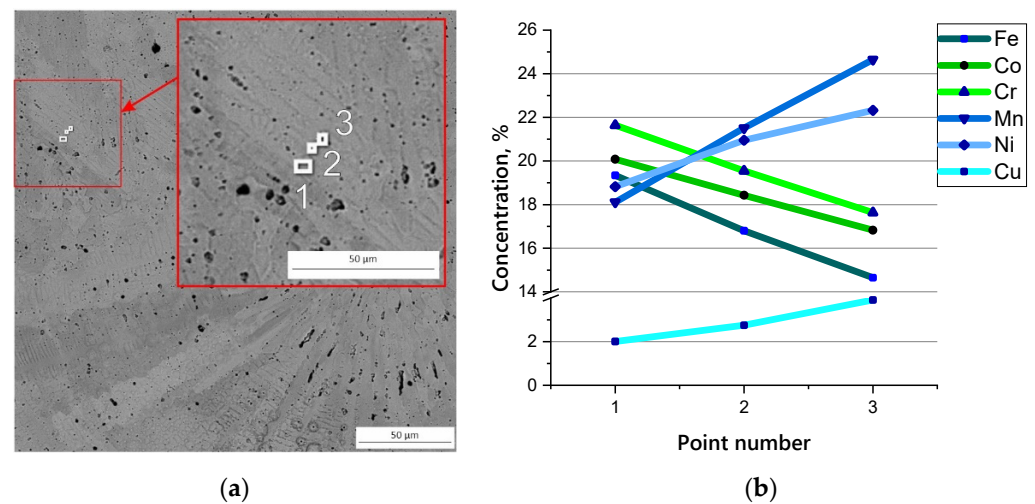


Figure 5. (a) The image of the sample section No. 1.1 through the SEM; (b) The concentration of elements at the points of this section.

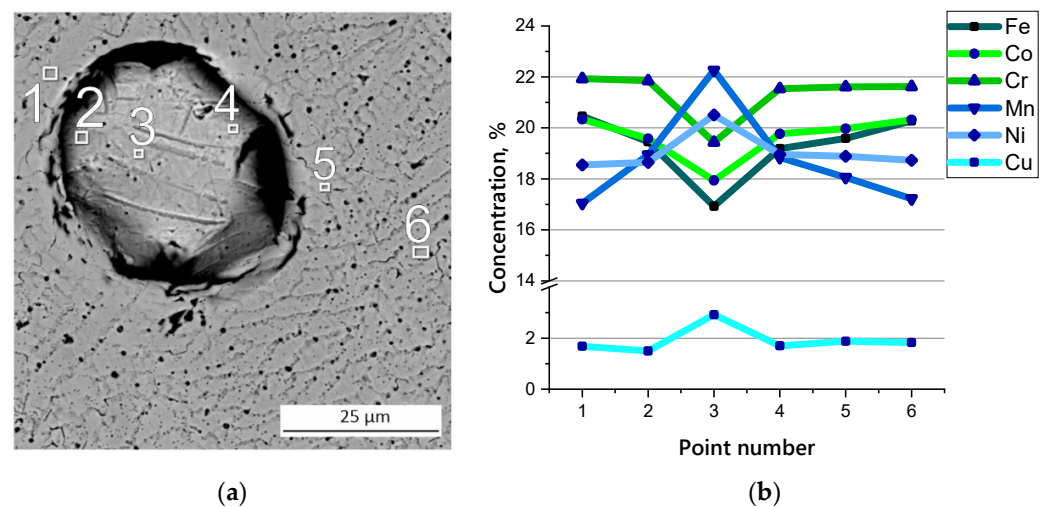


Figure 6. (a) The image of the sample section No. 2.1 through the SEM; (b) The concentration of elements at the points of this section.

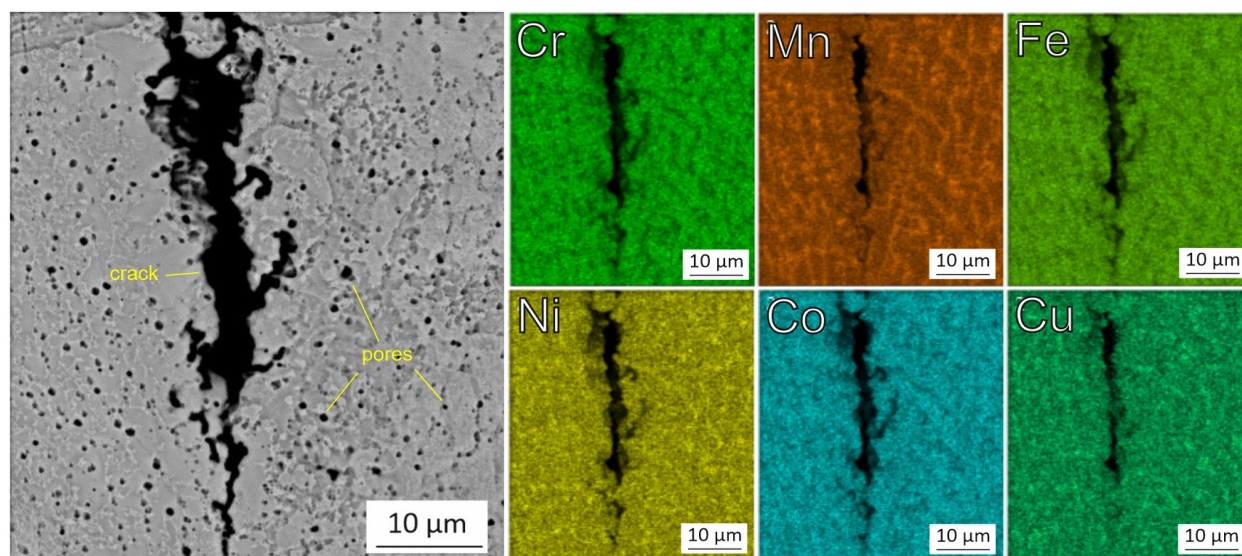


Figure 7. EDS analysis results for L-DED sample No. 2.1.

In sample No. 1.5, a high concentration of group B elements is observed along the crack boundaries. Presumably, this is because of the later release of these elements into the phase (see Section 3.1 of the Thermo-Calc calculation): after the crystallization of the elements of the first group A begins, less free space remains for the crystallization of the elements of the second group B from the liquid and therefore stresses arise between hardened surfaces of elements of the first group A, which leads to the formation of cracks.

Figure 5a shows the image of the sample section No. 1.1 through the SEM. Figure 5b shows a graph with similar behavior of the concentration of elements of groups A and B, which allows us to confirm this division into groups in sample No. 1.1. A graph was constructed with spectra 1, 2 and 3, which are read in sequentially. The graph illustrates how the percentage composition of spectrum 2 lies between spectra 1 and 3.

In sample No. 2.1, structural elements are observed, the size of which corresponds to the size of the particles of the initial powder and which have a rounded shape (Figure 6a). In structural elements of this type, there is a change in chemical composition from the center of the rounded elements to the edges (Figure 6b). The concentration of group B elements decreases from the center to the edges: Mn and Ni decrease from 22.3% and 20.5% to 18.5–19%, respectively, the Cu content decreases from 2.9% to 1.5–1.7%. This structural element may be the result of imperfection of the initial powder, in some particles of which group B elements predominate. And in combination with the minimum laser power during deposition, which is the lowest heating temperature in the experiment, the elements of group B simply did not have time to dissolve in group A due to the rapid crystallization of the elements of the latter group. Figure 7 also shows the division into areas A and B.

Visually comparing samples No. 2.1 and No. 1.5 (Figures 4 and 7) with the minimum and maximum laser power in the experiment, we come to the conclusion that with increasing laser power, the microstructure becomes larger. Accordingly, the areas of groups A and B are larger.

In sample No. 2.2, cracks spread along the boundaries of multidirectional dendrites (Figure 8). The determining factor in the direction of crack development is the orientation of dendrites. A change in the orientation of dendrite growth is observed, according to which the direction of crack propagation changes. The crack mainly runs along the boundaries of multidirectional dendrites. The reason is that at the final stage of solidification, liquid films are formed, which form an area with extremely low shear strength. These films exhibit a particularly strong effect at grain boundaries at a large angle. This phenomenon occurs when the secondary branches of one dendrite meet the secondary branches of another and block the flow of fluid to compensate for shrinkage depressions. Thus, cracking can occur

along grain boundaries at the last stage of solidification, which leads to the formation of an expanded region with low shear strength, in which the deformation is highly localized, which causes cracking under thermal stress [45,46]. The problem lies in the fact that the semi-solid substance also has low plasticity at the final stage of solidification, when the proportion of liquid is no longer high enough for the grains to move and rearrange themselves, adapting to the strain during stretching. This phenomenon occurs when the secondary branches of one dendrite meet the secondary branches of another and block the flow of fluid to compensate for shrinkage depressions. Thus, cracking can occur along grain boundaries at the last stage of solidification [47,48]. Cracks between dendrites in the same plane with a difference in directions with an angle of up to 45 degrees are noted in Figure 8.

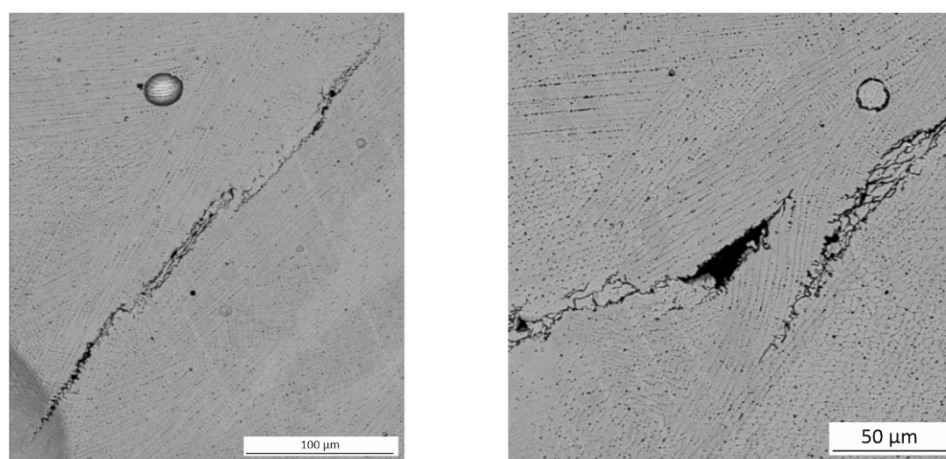


Figure 8. EDS analysis results for L-DED sample No. 2.2 with different magnifications.

In sample No. 2.3 (Figure 9a), the changes along and across the regions of unidirectional dendrites are insignificant, the composition dependence on the location of the point in the regions has not been revealed, however, points 1, 2 and 3 can be noted, which are distinguished by the composition (Figure 9b).

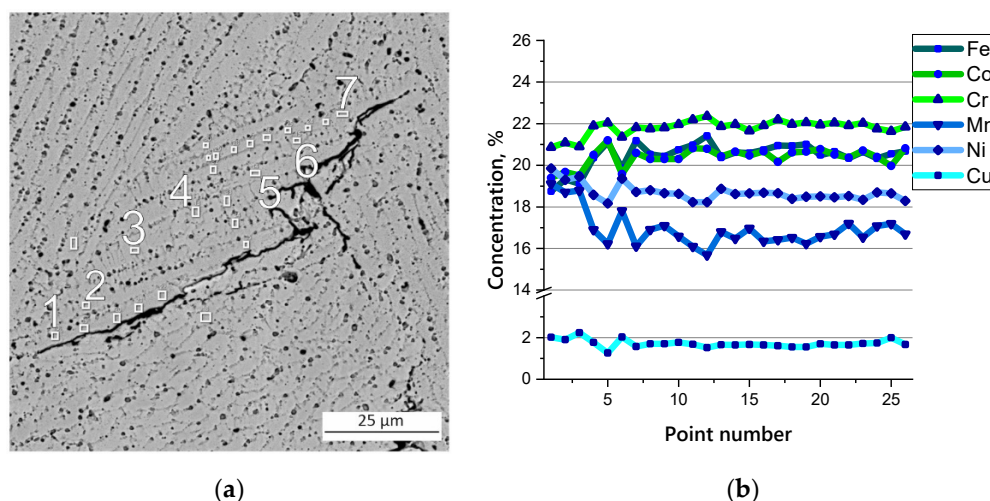


Figure 9. (a) The image of the sample section No. 2.3 through the SEM; (b) The concentration of elements at the points of this section.

In the samples of the second series, no changes in the microstructure were detected depending on the laser power (Figures 6, 8 and 9).

Figure 10 shows a plot for determining the chemical composition by points, depending on the considered areas A (points 1–3) and B (points 4–7) in Figure 10a and a diagram of the concentrations of elements in these areas for L-DED sample No. 1.1 in Figure 10b.

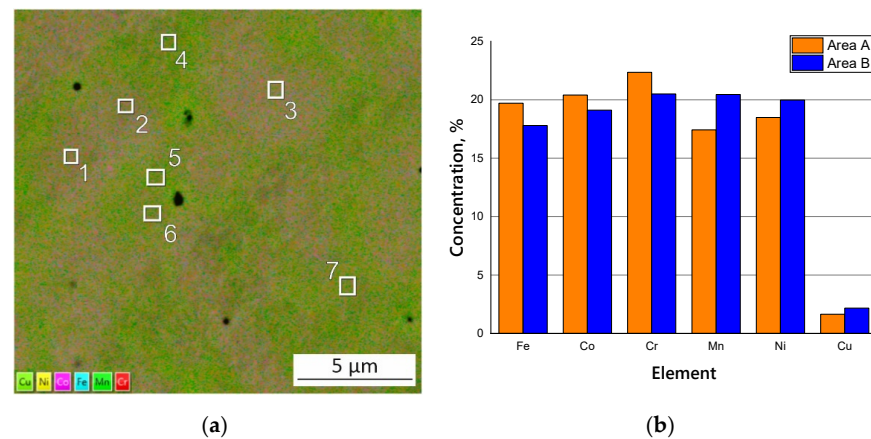


Figure 10. (a) The image of the sample section No. 1.1 through the SEM; (b) The concentration of elements in areas A and B of the section.

Based on the diagram above, we note that the concentrations of elements change in the selected areas A and B corresponding to the components of the increased concentration in the areas of elements of groups A and B.

3.3. Macrostructures of HEA

Figure 11 shows cross-sectional images of FeCoNiCrMn HEA samples of series 1.X. Only sample No. 1.1, which was built at minimum laser power, has no cracks. In the rest of the samples, cracks run vertically along the height of the sample, approximately in the center of the beads. Cracks in the samples go from 3–4 layers from the bottom. Single pores are present. With increasing laser power, the average pore size increases from 72 to 158 µm.

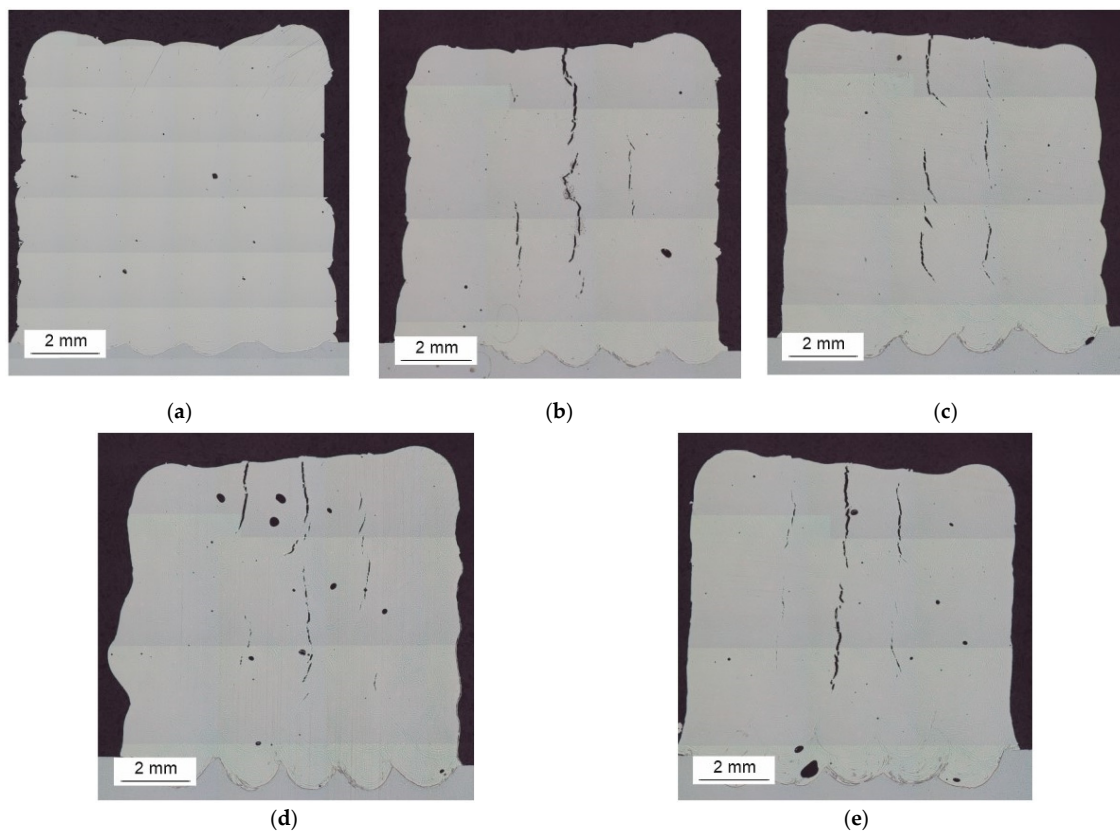


Figure 11. Optical Image of deposited FeCoNiCrMn cross-section: (a) Sample No. 1.1; (b) Sample No. 1.2; (c) Sample No. 1.3; (d) Sample No. 1.4; (e) Sample No. 1.5.

In the second series of depositing 2.X out of three samples, only sample No. 2.1 did not crack (Figure 12a–c). With increasing laser power, the size of pores and cracks increases. At the same time, cracks were formed not in the first layers, but above. There are pores whose size increases threefold with increasing laser power: from 34 to 99 μm .

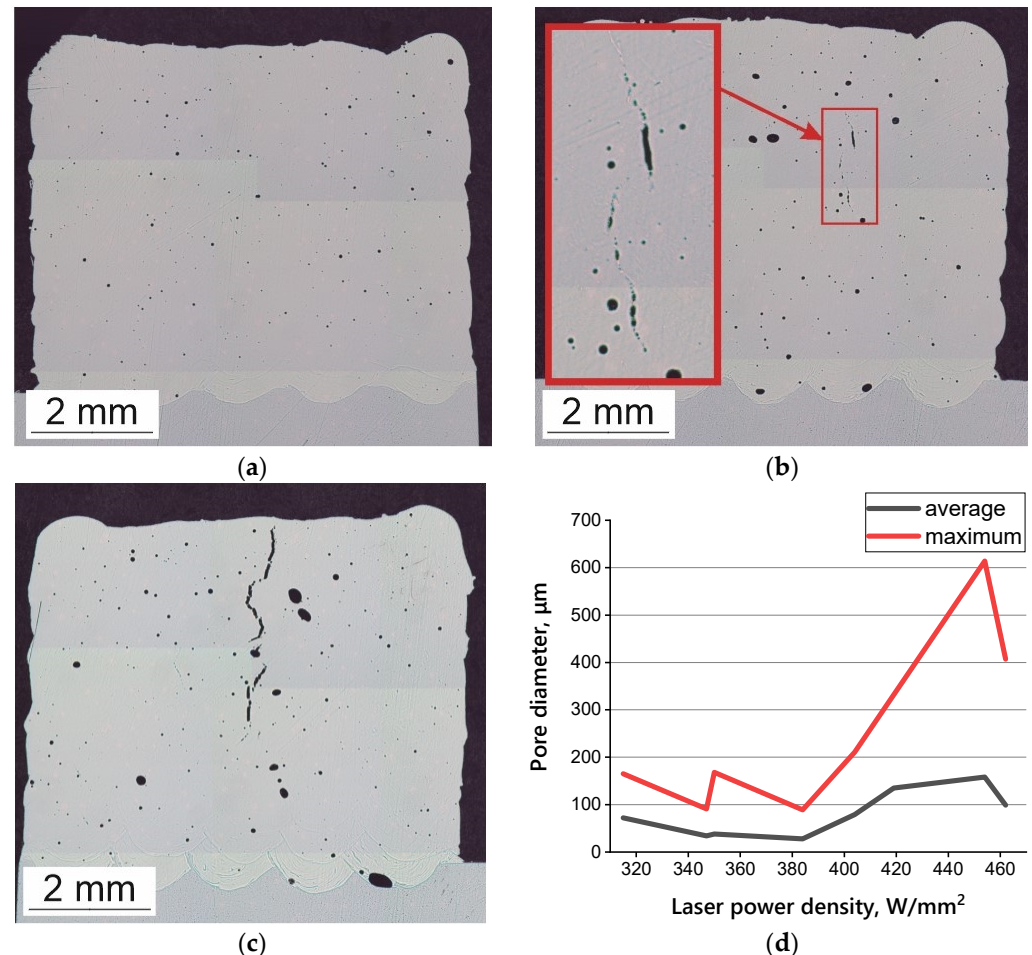


Figure 12. Optical Image of deposited FeCoNiCrMn cross-section: (a) Sample No. 2.1; (b) Sample No. 2.2; (c) Sample No. 2.3; (d) Graph of the dependence of pore size in two series on power density.

In two series, there is a tendency to increase the average and maximum pore size from the power density (Figure 12d). At the lowest power densities of 315 and 347 W/mm^2 , there are no cracks in the samples.

A higher power density means a greater temperature gradient in the deposited area, from which it can be concluded that at a power density of more than 350 W/mm^2 , the studied FeCoNiCrMn alloy is prone to cracking due to large residual stresses. Similarly, in each series, only samples with minimal laser power did not crack, and with increasing laser power, the temperature gradient increases, which leads to the formation of cracks.

There is also a tendency for a relative increase in the size of the detected cracks in length and width in relation to the laser power in the cross section of the samples.

3.4. Phase Composition Analysis

Figure 13 shows the XRD pattern for samples No. 1.1, No. 1.5, No. 2.1 and No. 2.3 having the maximum and minimum laser power in two series. The study confirmed an FCC structure, as was obtained at the modeling stage (Figure 2).

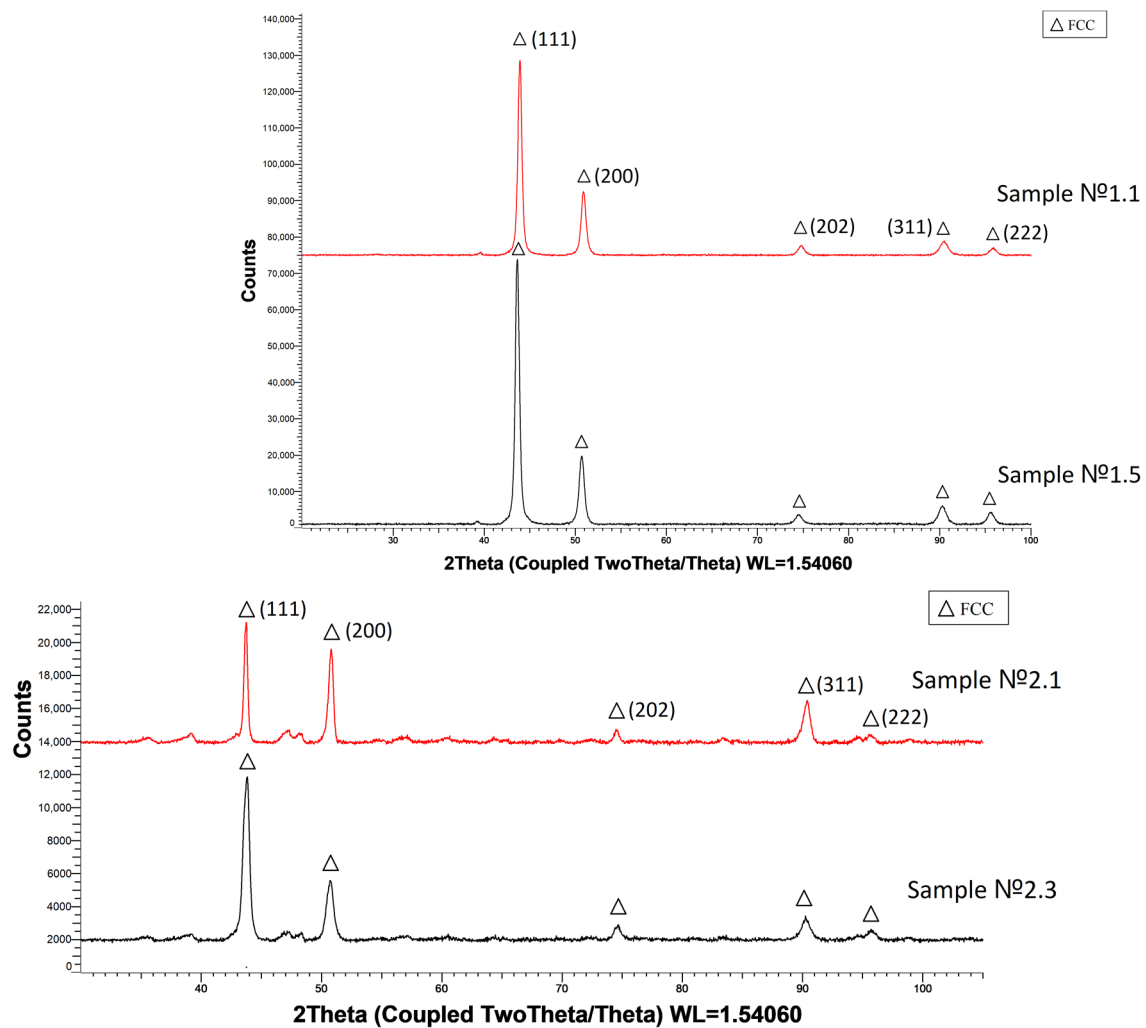


Figure 13. XRD patterns of samples No. 1.1, No. 1.5, No. 2.1 and No. 2.3.

With increasing laser power in the first series, there is an increase in the (111) peaks in height, which may mean an increase in the growth of the number of dendrites in these directions. Thus, an increase in the laser power leads to an increase in the number of dendrites in one direction. With increasing power in the second series, the growth of the (111) peak increases and the growth of the (200) peak decreases, indicating a change in the preferential growth of dendrites with a change in power.

3.5. Microhardness

Figure 14 shows the results of measuring the microhardness of all samples of the first and second series (Figure 14a) and scheme of points for measuring microhardness in the cross section of the samples (Figure 14b).

Values varied from 232 HV to 250 HV in the first series and from 237 HV to 265 HV in the second one. But in the top of the sample microhardness reduced down to 160–180 HV. It can be result from higher power and laser beam spot size, that led to the softer thermal cycle. Also in the top of samples material was not reheated, that would make possible for hardening.

Dependence of the average microhardness on power density was shown in Figure 15. It is evident that change of power density did not have strongly effect on microhardness.

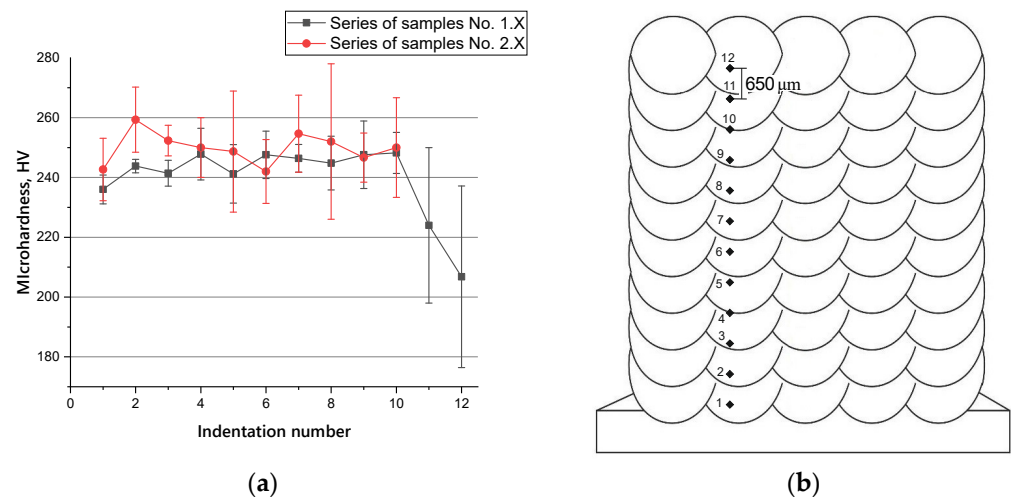


Figure 14. (a) Microhardness of samples; (b) Scheme of indentations for measuring microhardness in the cross section of the samples.

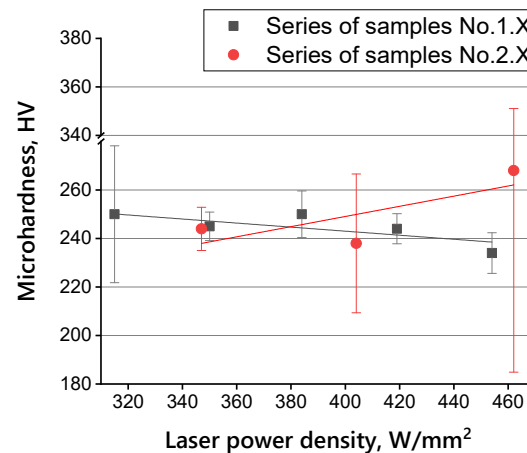


Figure 15. Dependence of microhardness on power density.

4. Discussion

By calculating the phase composition in the Thermo-Calc of the studied HEA with the composition of FeCoNiCrMn, the formation of a type of structure with a crystal lattice of FCC was predicted, which was experimentally confirmed by the results of XRD analysis.

During the simulation, two groups of elements were noted depending on the temperature at the beginning of the formation of the FCC phase: (Fe, Co, Cr) and (Mn, Ni, Cu). According to the results of microstructural analysis on SEM samples of FeCoNiCrMn, it is also possible to note the division into areas with an increased content of elements of these groups.

Figure 16 shows a diagram with the chemical compositions of the elements of areas A and B of the FeCoNiCrMn obtained HEA, and the extrapolated composition based on the results of modeling at room temperature 20 °C. Based on the figure, the extrapolation of the simulated composition is closer to the composition of area A.

Figure 17 shows a diagram with the chemical compositions of areas A and B of the obtained HEA FeCoNiCrMn and the temperature during the modeling of the phase composition corresponding to the closest possible values of the percentage composition of the elements. Based on the figure, the chemical compositions of the areas are closer to the simulated composition between 988–1294 °C, which is almost the entire simulated crystallization interval of the alloy. The resulting composition of area A has a smaller variation in coincidence with the temperature of the simulated composition: if cobalt is not considered, then the temperature coincidence interval will be from 1227 °C to 1287 °C.

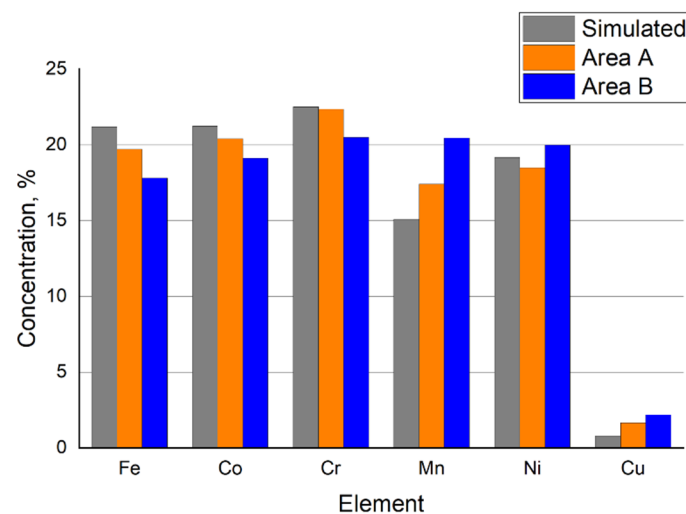


Figure 16. Diagram of the distribution of elements during modeling and the resulting alloy.

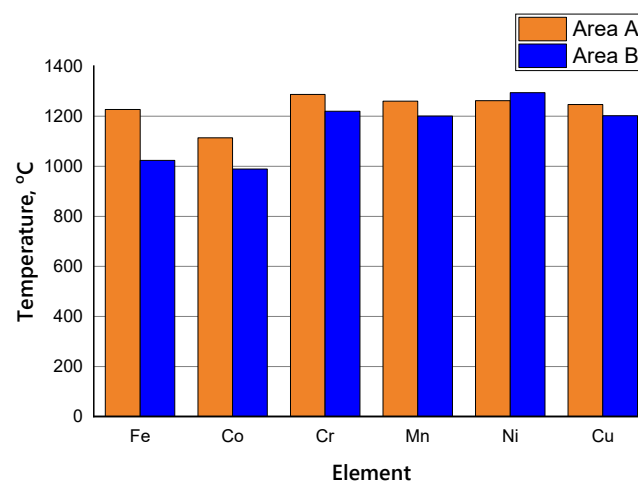


Figure 17. Diagram of the distribution of the elements of the resulting alloy and the temperature during modeling with the closest percentage composition to the resulting alloy.

The plans for the future are to study the behavior under load of the high-entropy alloy FeCrCoMnNi in a wide temperature range and to study the effect of replacing one main element in the high-entropy alloy FeCrCoMnNi under similar experimental conditions.

5. Conclusions

A high-entropy FeCoNiCrMn alloy has been successfully obtained by laser direct energy deposition. No cracks were found in the structure at the lowest power densities of 315 and 347 W/mm². In the other samples the cracks are located in height in the center of the beads. Single pores are observed in the structure of all samples. The average and maximum pore size is increase depending on the power density of laser radiation.

Areas with increased content of two groups of elements are observed In the samples: (Fe, Co, Cr) and (Mn, Ni, Cu). Cracks occur along the boundaries of multidirectional dendrites and between the dendrites in the same plane with a difference in directions with an angle of up to 45 degrees. In cracks there are mainly found elements of the group (Mn, Ni, Cu). As the laser power increases, the microstructure becomes larger.

Modeling in the Thermo-Calc software package showed that solid solutions with a crystal lattice of the FCC type are formed in alloys of the selected composition. A group of elements (Fe, Co, Cr) was noted in the common elements distribution in the FCC phase because of their greater concentration and sufficiently closer values of the molar content at the FCC phase formation beginning. According to the results of the SEM microstructural

analysis of the samples, the elements of the group (Fe, Co, Cr) are located together on the composition distribution maps, forming an area with an increased content of elements of this group.

The content of elements in the deposited alloy in the areas with a high content of elements (Fe, Co, Cr) is closer to the simulated alloy than in the areas with a high content of elements (Mn, Ni, Cu). In addition, the first area (Fe, Co, Cr) has smaller deviation from the crystallization temperature interval of the simulated alloy than the second one (Mn, Ni, Cu). If cobalt is not considered, the temperature intervals coincide between 1227 °C and 1287 °C, that is 42–84% of the crystallization interval.

The XRD patterns shows that with increasing laser power, the growth of the (111) peak increases, and the growth of the (200) peak decreases, which indicates a change in the dominant growth of dendrites with a change in laser power.

Hardness measurements showed uniform distribution of values on average, excepting the last points in the first series of samples. This change is because the last layer was not reheated and thermal cycle was softer than in the previous layers.

The power density can be used as a parameter to control pore formation process during the depositing a high-entropy FeCoNiCrMn alloy, since with increasing power density there is a tendency to increase both the size of pores and their amount. The same tendency was seen for cracks. However, no significant dependence was found for microhardness.

Author Contributions: Conceptualization, E.K.; methodology, E.K.; software, E.K.; validation, E.V., O.K.-K. and M.G.; formal analysis, E.K.; investigation, E.K. and I.K.; resources, I.K., O.K.-K. and M.G.; data curation, E.V.; writing—original draft preparation, E.K. and I.K.; writing—review and editing, E.K., E.V., O.K.-K. and M.G.; visualization, E.K. and I.K.; supervision, E.K.; project administration, E.K.; funding acquisition, E.V. and O.K.-K. All authors have read and agreed to the published version of the manuscript.

Funding: HEA synthesis is funded by the Ministry of Science and Higher Education of the Russian Federation as part of World-class Research Center program: Advanced Digital Technologies (contract No. 075-15-2022-312 dated 20.04.2022). Laser welding and structure research are funded by the the Russian Foundation for Basic Research (RFBR) within the framework of Development of a Reliable Joining Process for Dissimilar Intermetallic/Ni-based superalloy (Laser Welding/Brazing using High-Entropy Alloying Concept) [project number 20-53-56063].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, M.; Peng, Y.; Zhang, W.; Liu, Y.; Wang, L.; Hu, S.; Hu, Y. Gradient Distribution of Microstructures and Mechanical Properties in a FeCoCrNiMo High-Entropy Alloy during Spark Plasma Sintering. *Metals* **2019**, *9*, 351. [\[CrossRef\]](#)
2. Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H.; Chang, S.-Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303. [\[CrossRef\]](#)
3. Zhang, Y.; Zuo, T.T.; Tang, Z.; Gao, M.C.; Dahmen, K.A.; Liaw, P.K.; Lu, Z.P. Microstructures and properties of high-entropy alloys. *Prog. Mater. Sci.* **2014**, *61*, 1–93. [\[CrossRef\]](#)
4. He, J.Y.; Wang, H.; Huang, H.L.; Xu, X.D.; Chen, M.W.; Wu, Y.; Liu, X.J.; Nieh, T.G.; An, K.; Lu, Z.P. A precipitation-hardened high-entropy alloy with outstanding tensile properties. *Acta Mater.* **2016**, *102*, 187–196. [\[CrossRef\]](#)
5. Jiang, W.; Zhu, Y.; Zhao, Y. Mechanical Properties and Deformation Mechanisms of Heterostructured High-Entropy and Medium-Entropy Alloys: A Review. *Front. Mater.* **2022**, *8*, 530. [\[CrossRef\]](#)
6. Wang, Z.; Fang, Q.; Li, J.; Liu, B.; Liu, Y. Effect of lattice distortion on solid solution strengthening of BCC high-entropy alloys. *J. Mater. Sci. Technol.* **2017**, *34*, 349–354. [\[CrossRef\]](#)
7. Zhang, Y.; Yan, X.; Ma, J.; Lu, Z.; Zhao, Y. Compositional gradient films constructed by sputtering in a multicomponent Ti–Al–(Cr, Fe, Ni) system. *J. Mater. Res.* **2018**, *33*, 3330–3338. [\[CrossRef\]](#)
8. Sebastian, A.K.; Schroers, J. Metastability in high entropy alloys. *Scr. Mater.* **2020**, *186*, 392–400.

9. Shim, S.H.; Moon, J.; Pouraliakbar, H.; Lee, B.J.; Hong, S.I.; Kim, H.S. Toward excellent tensile properties of nitrogen-doped CoCrFeMnNi high-entropy alloy at room and cryogenic temperatures. *J. Alloys Compd.* **2022**, *897*, 163217. [\[CrossRef\]](#)
10. Rizi, M.S.; Minouei, H.; Lee, B.J.; Toroghinejad, M.R.; Hong, S.I. Effects of carbon and molybdenum on the nanostructural evolution and strength/ductility trade-off in Fe₄₀Mn₄₀Co₁₀Cr₁₀ high-entropy alloys. *J. Alloys Compd.* **2022**, *911*, 165108. [\[CrossRef\]](#)
11. Pogrebnyak, A.D.; Bagdasaryan, A.A.; Yakushchenko, I.V.; Beresnev, V.M. The structure and properties of high-entropy alloys and nitride coatings based on them. *Russ. Chem. Rev.* **2014**, *83*, 1027–1061. [\[CrossRef\]](#)
12. Sreeramagiri, P.; Roy, A.; Balasubramanian, G. Effect of Cooling Rate on the Phase Formation of AlCoCrFeNi High-Entropy Alloy. *J. Phase Equilibria Diffus.* **2021**, *42*, 772–780. [\[CrossRef\]](#)
13. Singh, P.; Smirnov, A.V.; Johnson, D.D. Atomic Short-Range Order and Incipient Long-Range Order in High-Entropy Alloys. *Phys. Rev. B* **2015**, *91*, 204–224. [\[CrossRef\]](#)
14. Ma, L.; Gao, Z.; Hu, S.; Zeng, Z.; Xu, J.; Wang, J. Effect of Cooling Rate on Microstructure and Mechanical Properties of Al_{0.3}CoCrFeNi High-Entropy Alloy. *Mater. Res. Express* **2019**, *6*, 56–540. [\[CrossRef\]](#)
15. Li, C.; Zhao, M.; Li, J.C.; Jiang, Q. B2 Structure of High-Entropy Alloys with Addition of Al. *J. Appl. Phys.* **2008**, *104*, 113–504. [\[CrossRef\]](#)
16. Chen, J.; Jiang, X.; Sun, H.; Shao, Z.; Fang, Y.; Shu, R. Phase transformation and strengthening mechanisms of nanostructured high-entropy alloys. *Nanotechnol. Rev.* **2021**, *10*, 1116–1139. [\[CrossRef\]](#)
17. Molnár, D.; Vida, A.; Huang, S.; Chinh, N.Q. The effect of cooling rate on the microstructure and mechanical properties of NiCoFeCrGa high-entropy alloy. *J. Mater. Sci.* **2019**, *54*, 5074–5082. [\[CrossRef\]](#)
18. Jablonski, P.D.; Licavoli, J.J.; Gao, M.C.; Hawk, J.A. Manufacturing of high entropy alloys. *JOM* **2015**, *67*, 2278–2287. [\[CrossRef\]](#)
19. Ma, L.; Li, C.; Jiang, Y.; Zhou, J.; Wang, L.; Wang, F.; Tangqing, C.; Xue, Y. Cooling rate-dependent microstructure and mechanical properties of Al_xSi_{0.2}CrFeCoNiCu_{1-x} high entropy alloys. *J. Alloys Compd.* **2017**, *694*, 61–67. [\[CrossRef\]](#)
20. Lv, Y.; Hu, R.; Yao, Z.; Xu, D.; Liu, Y.; Fan, X. Cooling rate effect on microstructure and mechanical properties of Al_xCoCrFeNi high entropy alloys. *Mater. Des.* **2017**, *132*, 392–399. [\[CrossRef\]](#)
21. Kalali, D.; Antharam, S.; Hasan, M.; Pidatla, S.K.; Phani, P.S.; Rao, K.B.S.; Rajulapati, K.V. On the origins of ultra-high hardness and strain gradient plasticity in multiphase nanocrystalline MoNbTaTiW based refractory high-entropy alloy. *Mater. Sci. Eng. A* **2021**, *812*, 141098. [\[CrossRef\]](#)
22. Zhou, Y.; Zhang, Z.; Wang, D.; Xiao, W.; Ju, J.; Liu, S.; Xiao, B.; Yan, M.; Yang, T. New trends in additive manufacturing of high-entropy alloys and alloy design by machine learning: From single-phase to multiphase systems. *J. Mater. Inform.* **2022**, *2*, 18. [\[CrossRef\]](#)
23. Perrin, A.E.; Schuh, C.A. Stabilized nanocrystalline alloys: The intersection of grain boundary segregation with processing science. *Annu. Rev. Mater. Res.* **2021**, *51*, 68. [\[CrossRef\]](#)
24. Bennett, J.L.; Kafka, O.L.; Liao, H.; Wolff, S.; Yu, C.; Cheng, P.; Hyatt, G.; Ehmann, K.; Cao, J. Cooling rate effect on tensile strength of laser deposited Inconel 718. *Procedia Manuf.* **2018**, *26*, 912–919. [\[CrossRef\]](#)
25. Pauly, S.; Wang, P.; Kuhn, U.; Kosiba, K. Experimental determination of cooling rates in selectively laser-melted eu-tectic Al-33Cu. *Addit. Manuf.* **2018**, *22*, 753–757.
26. Zhang, J.; Jia, T.; Qiu, H.; Zhu, H.; Xie, Z. Effect of cooling rate upon the microstructure and mechanical properties of in-situ TiC reinforced high entropy alloy CoCrFeNi. *J. Mater. Sci. Technol.* **2020**, *42*, 122–129. [\[CrossRef\]](#)
27. Derimow, N.; Clark, T.; Abbaschian, R. Solidification processing and cooling rate effects on hexagonal Co₂₂Cr₁₈Cu₂₀Mn₁₆Ti₂₄ high-entropy alloys. *Mater. Chem. Phys.* **2020**, *240*, 122–188. [\[CrossRef\]](#)
28. Dada, M.; Popoola, P.; Mathe, N.; Pityana, S.; Adeosun, S.; Aramide, O.; Lengopeng, T. Process optimization of high entropy alloys by laser additive manufacturing. *Eng. Rep.* **2020**, *2*, e12252. [\[CrossRef\]](#)
29. Mahmood, M.A.; Alabtah, F.G.; Hamidi, Y.A.; Khraisheh, M. On Laser Additive Manufacturing of High-entropy Alloys: A Critical Assessment of In-situ Monitoring Techniques and Their Suitability. *Mater. Des.* **2023**, *226*, 1111658. [\[CrossRef\]](#)
30. Gorsse, S.; Hutchinson, C.; Gouné, M.; Banerjee, R. Additive manufacturing of metals: A brief review of the characteristic microstructures and properties of steels, Ti-6Al-4V and high-entropy alloys. *Sci. Technol. Adv. Mater.* **2017**, *18*, 584–610. [\[CrossRef\]](#)
31. Löbel, M.; Lindner, T.; Mehner, T.; Lampke, T. Influence of titanium on microstructure, phase formation and wear behaviour of AlCoCrFeNiTi_x high-entropy alloy. *Entropy* **2018**, *20*, 505. [\[CrossRef\]](#)
32. Shun, T.-T.; Hung, C.-H.; Lee, C.-F. Formation of ordered/disordered nanoparticles in FCC high entropy alloys. *J. Alloys Compd.* **2010**, *493*, 105–109. [\[CrossRef\]](#)
33. Chen, S.; Xie, X.; Li, W.; Feng, R.; Chen, B.; Qiao, J.; Ren, Y.; Zhang, Y.; Dahmen, K.A.; Liaw, P.K. Temperature effects on the serrated behavior of an Al_{0.5}CoCrCuFeNi high-entropy alloy. *Mater. Chem. Phys.* **2017**, *210*, 20–28. [\[CrossRef\]](#)
34. Sriharitha, R.; Murty, B.; Kottada, R.S. Phase formation in mechanically alloyed Al_xCoCrCuFeNi (x = 0.45, 1, 2.5, 5 Mol) high entropy alloys. *Intermetallics* **2013**, *32*, 119–126. [\[CrossRef\]](#)
35. Xiang, S.; Luan, H.; Wu, J.; Yao, K.-F.; Li, J.; Liu, X.; Tian, Y.; Mao, W.; Bai, H.; Le, G.; et al. Microstructures and mechanical properties of CrMnFeCoNi high entropy alloys fabricated using laser metal deposition technique. *J. Alloys Compd.* **2019**, *773*, 387–392. [\[CrossRef\]](#)
36. Stavridis, J.; Papacharalampopoulos, A.; Stavropoulos, P. Quality assessment in laser welding: A critical review. *Int. J. Adv. Manuf. Technol.* **2017**, *94*, 1825–1847. [\[CrossRef\]](#)

37. Gao, X.; Yu, Z.; Hu, W.; Lu, Y.; Zhu, Z.; Ji, Y.; Lu, Y.; Qin, Z.; Lu, X. In situ strengthening of CrMnFeCoNi high-entropy alloy with Al realized by laser additive manufacturing. *J. Alloys Compd.* **2020**, *847*, 156563. [\[CrossRef\]](#)
38. Tong, Z.; Ren, X.; Jiao, J.; Zhou, W.; Ren, Y.; Ye, Y.; Larson, E.A.; Gu, J. Laser additive manufacturing of FeCrCoMnNi high-entropy alloy: Effect of heat treatment on microstructure, residual stress and mechanical property. *J. Alloys Compd.* **2019**, *785*, 1144–1159. [\[CrossRef\]](#)
39. Savinov, R.; Wang, Y.; Wang, J.; Shi, J. Comparison of microstructure and properties of CoCrFeMnNi high-entropy alloy from selective laser melting and directed energy deposition processes. *Procedia Manuf.* **2021**, *53*, 435–442. [\[CrossRef\]](#)
40. Fiochi, J.; Casati, R.; Tuissi, A.; Biffi, C.A. Laser Beam Welding of CoCuFeMnNi High Entropy Alloy: Processing, Microstructure, and Mechanical Properties. *Adv. Eng. Mater.* **2022**, *24*, 2200523. [\[CrossRef\]](#)
41. Shao, J.; Yu, G.; He, X.; Li, S.; Chen, R.; Zhao, Y. Grain size evolution under different cooling rate in laser additive manufacturing of superalloy. *Opt. Laser Technol.* **2019**, *119*, 105662. [\[CrossRef\]](#)
42. Dong, B.; Wang, Z.; Zhu, H.; Muránsky, O.; Qiu, Z.; Shen, C.; Pan, Z.; Li, H. Low neutron cross-section FeCrVTiNi based high-entropy alloys: Design, additive manufacturing and characterization. *Microstruct. J.* **2022**, *2*, 2022003. [\[CrossRef\]](#)
43. Bocklund, B.; Bobbio, L.D.; Otis, R.A.; Beese, A.M.; Liu, Z.K. Experimental validation of Scheil–Gulliver simulations for gradient path planning in additively manufactured functionally graded materials. *Materialia* **2020**, *11*, 100689. [\[CrossRef\]](#)
44. Bocklund, B.; Bobbio, L.; Otis, R.A.; Beese, A.M.; Liu, Z.-K. Scheil–Gulliver simulations for the design of functionally graded alloys by additive manufacturing using pycalphad. *arXiv* **2020**, arXiv:2001.11611.
45. Wang, N.; Mokadem, S.; Rappaz, M.; Kurz, W. Solidification cracking of superalloy single- and bi-crystals. *Acta Mater.* **2004**, *52*, 3173–3182. [\[CrossRef\]](#)
46. Wang, C.; Yu, J.; Zhang, Y.; Yu, Y. Phase evolution and solidification cracking sensibility in laser remelting treatment of the plasma-sprayed CrMnFeCoNi high entropy alloy coating. *Mater. Des.* **2019**, *182*, 108040. [\[CrossRef\]](#)
47. Kou, S. A criterion for cracking during solidification. *Acta Mater.* **2015**, *88*, 366–374. [\[CrossRef\]](#)
48. Coniglio, N.; Cross, C.E. Initiation and growth mechanisms for weld solidification cracking. *Int. Mater. Rev.* **2013**, *7*, 375–397. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.