

Article

Microstructure and Mechanical Properties of High-Entropy Alloy FeCoNiCr(X) Produced by Laser Directed Energy Deposition Process: Effect of Compositional Changes

Ekaterina Kovalenko , Igor Krasanov , Ekaterina Valdaytseva, Stanislav Stankevich, Olga Klimova-Korsmik  and Marina Gushchina 

World-Class Research Center “Advanced Digital Technologies”, State Marine Technical University, 190121 Saint Petersburg, Russia; igor.krasanov.99@mail.ru (I.K.); laser@corp.smtu.ru (E.V.); s.stankevich@ilwt.smtu.ru (S.S.); o.klimova@ltc.ru (O.K.-K.); gushchina_mo@corp.smtu.ru (M.G.)

* Correspondence: kovalenko.ek@inbox.ru

Abstract: High-entropy alloys (HEAs) have shown promise as materials with improved mechanical properties compared to traditional materials. Achieving the desired mechanical properties depends on the alloy composition, both in terms of percentage and elements. Laser directed energy deposition technology allows for the production of products with various complex geometries and dimensions (L-DED). It has been found that HEA FeCoNiCrCu alloys can be divided into regions with high concentrations of Fe + Co + Cr and Cu elements. Dendrite growth directions of HEA FeCoNiCrCu are (111) and (200), and the average microhardness is around 240 HV. All samples have cracks vertically along the height. Fine-grained and dendrite structures were observed. Cu-element is mainly found in cracks. The HEA FeCoNiCrCu alloy was compared with another HEA FeCoCrMnNi, successfully obtained by the same L-DED technology. Comparing the two HEAs FeCoNiCrCu and FeCoCrMnNi obtained with the same deposition parameters can help determine the impact of one element on the phase composition, microstructure and mechanical properties of the high-entropy alloy. Replacing the element Mn with Cu in HEA FeCoNiCrMn led to a shift in the dendrite growth from one to two predominant directions and a decrease in the average microhardness by 20%.

Keywords: high-entropy alloys; additive technologies; laser directed energy deposition; microstructure; mechanical properties



Academic Editor: Qingping Cao

Received: 25 November 2024

Revised: 20 December 2024

Accepted: 29 December 2024

Published: 31 December 2024

Citation: Kovalenko, E.; Krasanov, I.; Valdaytseva, E.; Stankevich, S.; Klimova-Korsmik, O.; Gushchina, M. Microstructure and Mechanical Properties of High-Entropy Alloy FeCoNiCr(X) Produced by Laser Directed Energy Deposition Process: Effect of Compositional Changes. *Metals* **2025**, *15*, 26. <https://doi.org/10.3390/met15010026>

Copyright: © 2024 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/>).

1. Introduction

High-entropy alloys (HEAs) are a class of materials defined as solid solution alloys that contain more than five principal elements in equal or near equal atomic ratio, which makes the formation of simple solid solution phase easier [1,2]. The alloy composition affects the absence of an intermetallic compound and building a single solid solution, having different types of phases: FCC, BCC or FCC + BCC [2]. HEAs attract attention as a promising material, due to high strength, low electrical conductivity and good resistance to oxidation and corrosion [3]. Due to their excellent balance of exceptional fractured toughness and yielding strength, HEAs have a greater threshold of breakage [4].

The properties of HEAs are determined by their phase and elemental composition. Elemental composition is a critical factor in alloy design, which will definitely affect the alloying behaviors and phase composition of HEAs. Such a large number of elements in the alloy ensures the mechanical characteristics of the alloys are higher in value than those

predicted by the mixing rule [5]. Experimental evidence proved in the synthesis of HEAs that Cu, Ni, Mn and Co elements favor the generation of FCC solid-solution phases, while Al, Cr, W, V and Ti elements promote the formation of BCC phases [6–9]. HEAs with a BCC type crystal lattice have high strength, and HEAs with an FCC type crystal lattice have high plasticity [10]. In [3], a phase transition was obtained between FCC and FCC + BCC with increasing concentration of Al in HEA $\text{Al}_x\text{FeCoCrNiCu}$. The microhardness of alloys increased from 165 to 485 HV with the addition of Al from $x = 0.25$ to 1.0. In [2], decreasing microhardness with increasing concentration of Cr, Fe, Co and Ni was obtained in HEA $\text{Al}_x\text{CrFeCoNi}$. Addition of Al was identified to exert significant effects on the structural formation and physical properties of HEAs due to its relatively larger atomic radius. In [5], the alloy without Al addition was mainly composed of FCC solid-solution while the main phase transformed stabilized BCC solid-solution as Al was introduced.

Laser directed energy deposition (L-DED) is carried out by the interaction of material with laser radiation. L-DED is characterized by a rapid laser solidification process, which is non-equilibrium and avoids component segregation. Due to the high temperature gradient in the L-DED, the deposited direction of columnar grains is perpendicular to the interface and with the decreasing temperature gradient in the center of beads, the columnar grains turn into equiaxed grains, as shown in [11–14].

The FeCoNiCrCu alloy has previously been obtained in other works and has been studied. In [15], a high-entropy alloy FeCoNiCrCuX ($X = 0, 0.5, 1.0$ and 1.5) was deposited using Laser cladding technology in order to study Cu for microstructure and properties. With an increase in the concentration of Cu in the alloy, the average atomic radius will increase from 1.236 Å to 1.281 Å. The paper notes that Cu is mainly segregated at the grain boundary, and the degree of segregation of the Cu element at the grain boundaries will increase as its content increases. Increasing the concentration of Cu reduces the average hardness from 270.1 HV to 263.6 HV. However, due to the influence of the steel substrate in the form of mixing in the first layers of the substrate material and powder, the FeCoCrNiCuX in this study refers to an alloy with medium entropy. In [16], the CoCrCuFeNi HEA coating was obtained by laser deposition to study its heat resistance and the possibility of using it at high temperatures. The approved alloy has a dendritic structure. The composition changed slightly after annealing, and in particular, Cu enrichment and Cr depletion were more evident in the interdendritic phase. In addition, Ni was less noticeable in the interdendritic phase, and Fe was less noticeable in the dendritic phase. The change in composition certainly affected the arrangement of atoms in the alloy and is believed to have led to a decrease in the lattice constant. The atomic rearrangement may very well have weakened some lattice deformation caused by the dissolution of the solid. In [17], it is noted that the atoms of dissolved Cu tend to segregate in the form of an interdendritic phase, and the corrosion rate of the alloy during annealing gradually decreases as the annealing temperature increases from 350 to 1350 °C. In [18], HEA CoCrCuFeNi is prepared from the high purity elemental powders by mechanical alloying. Mechanically alloyed powder samples are subsequently annealed at different temperatures. It is established that the single phase of FCC is thermally stable up to 800 °C, and then it splits into two phases of FCC. One of the phases of FCC is rich in Cu. In [19], the good wear resistance and high hardness of the CoCrCuFeNi alloy are attributed to the addition of Cu.

In [20–24], HEAs with a difference in composition in one element were studied. Structural and magnetic properties are mainly studied in such works as [20–22], and work can also be found studying chemical and lattice inhomogeneous distributions, elemental composition, mechanical and tribological properties [23,24]. In these works, other methods of production are used, such as cast, vacuum arc melting and wire arc additive technology (WAAM).

The study aims to understand the extent of influence of one element on the mechanical properties and microstructure of an HEA obtained by the L-DED method in order to be able to predict the properties of the material before deposition. In this work, to analyze the effect of one element in the high-entropy alloy on changes in structure, phase and chemical composition under the same conditions, an HEA FeCoNiCrCu was obtained by replacing Mn with Cu in the previously successfully deposited HEA FeCoNiCrMn by the same L-DED method with the same deposition parameters [25].

2. Materials and Methods

To obtain samples of the HEA by L-DED technology, the FeCoNiCrCu powder produced by gas atomization technology. The chemical composition of the powder in weight percentages was determined using a Tescan Mira3 scanning electron microscope (SEM) (TESCAN, Brno, Czech Republic) using EDS analysis console Aztec Live Advanced Ultim Max 65 (Oxford Instruments NanoAnalysis, Wycombe, UK) energy dispersive microanalysis system point-by-point on a powder slice (Table 1). The size of powder is 50–200 μm .

Table 1. Chemical composition of FeCoNiCrCu powder (at.%).

Cr	Fe	Co	Ni	Cu
17.5	21.85	20.35	20.5	19.8

A series of samples were built using an L-DED 3D printing machine (ILIST-S) produced by Institute of Laser and Welding Technology (Saint Petersburg Marine Technical University, Saint Petersburg, Russia) (Figure 1a). The complex includes industrial robot LRM-M20iB/25 (Fanuc, Oshino-mura, Japan), fiber laser LS-3 Yb (IPG Photonics, Oxford, MA, USA), head for laser deposition FLW D30 (IPG Photonics, Oxford, MA, USA), nozzle SO12 (SPbSMTU, St. Petersburg, Russia), powder feeder (Oerlikon, Freienbach, Switzerland). Figure 1b shows the FeCoNiCrCu powder, which was used for deposition of samples. Figure 1c shows the scheme of deposited samples.

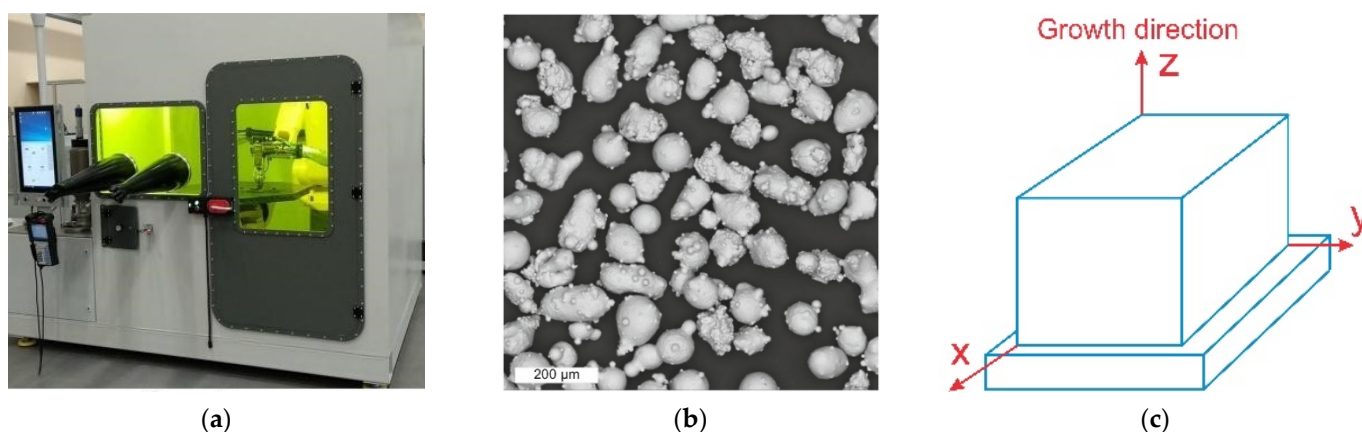


Figure 1. (a) 3D printer used for the current work; (b) FeCoNiCrCu powder; (c) the scheme of deposited samples.

Deposition was carried out in a sealed chamber in an argon atmosphere. Argon is a transporting gas here. For the study, five samples HEA FeCoNiCrCu were deposited with changing the laser power: 1.8–2.6 kW. The values of laser power were taken similarly to previous work on HEA FeCoNiCrMn deposition to obtain the most accurate results for comparison [25]. The range of values of laser power will allow us to track the trend in microstructure development and mechanical properties at various cooling rates. Higher

laser power, with other parameters remaining the same, leads to lower cooling rates. The parameters of deposition by the L-DED method and the size of samples are presented in Table 2.

Table 2. Laser directed energy deposition parameters.

Sample Number	Laser Power, kW	Spot Size, mm	Bead Width, mm	Sample Size, mm	Scanning Speed, mm/s	Layer Height, mm
1	1.8	2.7	2.5	Height: 9 Width: 8	25	0.8
2	2.0					
3	2.2					
4	2.4					
5	2.6					

Sample preparation was performed using grinding sandpapers with step-by-step reduction in the grit size, from P180 to P1200. Polishing was performed on special polishing cloths using diamond suspension with the size of the diamond particles being 9 and 3 μm and 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. Samples were also etched with HCl and HNO_3 mixed in a 3:1 ratio. Microstructure of the samples were investigated with a DMI 5000 optical microscope (Leica, Wetzlar, Germany) using the “Axalit” program (Axalit, Ekaterinburg, Russia). Energy dispersive X-ray spectroscopy (EDX) was carried out on a polished surface of the specimen using a Tescan Mira3 (TESCAN, Brno, Czech Republic) scanning electron microscope (SEM) with AZtecLive Advanced Ultim Max 65 (Oxford Instruments NanoAnalysis, Wycombe, UK) EDS system. The grain orientation in the printed sample was investigated using an Electron Backscattered Diffraction (EBSD) detector C-Nano with HKL database, software AZtec 6.0 (Oxford Instruments NanoAnalysis, Wycombe, UK), and Oxford Advanced Ultim Max 65 energy dispersive microanalysis system. X-ray diffraction (XRD) was performed using a Bruker D2 Phaser (Bruker, Karlsruhe, Germany) diffractometer with Cu $\text{K}\alpha$ radiation measured at 2θ from 20° to 100° , operating at 30 kV and 10 mA with a 2θ step size of 0.02° and exposure time of 0.1 s. Vickers microhardness was determined by applying a 300 g load for 10 s with a Future FM-310 microhardness tester (FUTURE-TECH CORP, Kawasaki, Japan). The indentations were applied over the entire height of the samples, starting from the substrate. For the study, 10 indentations were made and the distance between them was 650 μm . This distance was chosen in order to get the measures from all beds along the height of the samples.

3. Results and Discussion

3.1. Macrostructures of HEA

Figure 2 shows cross-sectional optical images of deposited HEA FeCoNiCrCu with different deposition parameters. All samples have cracks, which run vertically along the height of the samples, approximately in the center of the beads. Hot cracks are a common defect in L-DED technology. Samples have also shown the presence of non-fusion and characteristic pores associated with L-DED. Non-fusion was detected only in Sample No. 1 with the lowest laser power: the defects listed above are also typical for L-DED products [26]. Non-fusion may occur due to insufficient time in the liquid phase of the material. Single pores are present in all samples. These small single pores are typical in products produced by the L-DED method.

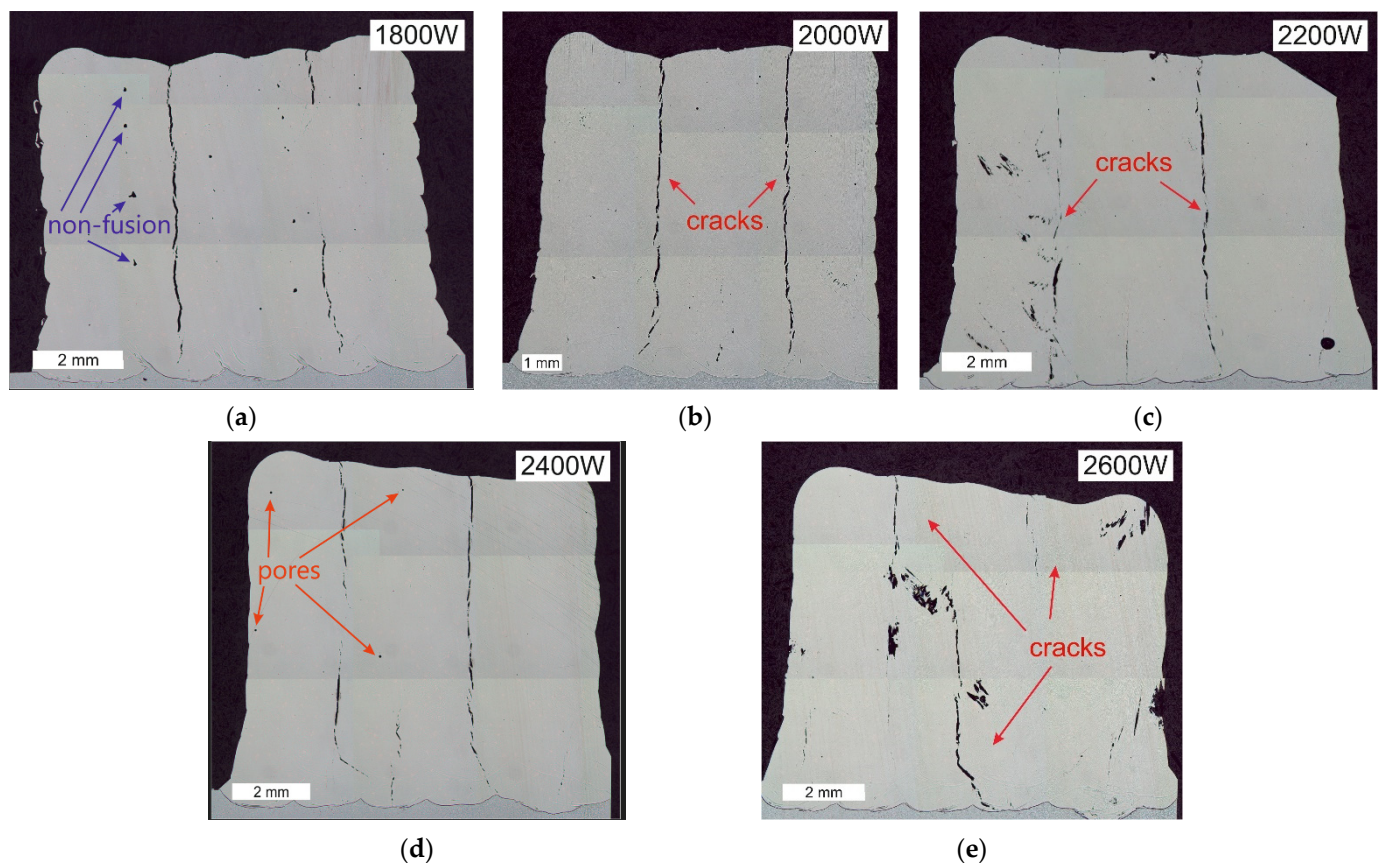


Figure 2. Optical image of deposited FeCoNiCrCu cross-section: (a) Sample No. 1; (b) Sample No. 2; (c) Sample No. 3; (d) Sample No. 4; (e) Sample No. 5.

Comparing HEA FeCoNiCrCu with HEA FeCoNiCrMn [25] reveals the following: the cracks have a similar location and cracks have a large extent in cross-section; visually, the number and size of pores are smaller. Samples No. 2–5 also are cracked. Sample No. 1 with the lowest laser power is cracked whereas Sample No. 1 HEA FeCoNiCrMn is not cracked. Thus, the deposition parameters for Sample No. 1 are optimal for HEA FeCoNiCrMn, but have too much heat input for HEA FeCoNiCrCu.

3.2. Microstructure and Chemical Composition of HEA

Figure 3 shows an SEM image of the microstructure of Sample No. 1 HEA FeCoNiCrCu. In this image, we can see two distinctive areas: grain area (Figure 3B) and dendritic area (Figure 3C). We can also see a layer rich with Cu on Figure 3A.

Chemical deposition of those areas is represented in Table 3. As we can see from it, light mesh between grains and interdendritic space contains more Cu than grains and dendrites. The reason for this could be that Cu reduces the melting point of the alloy and the areas poor with Cu crystallizes earlier, forcing the rest of the alloy, rich with Cu, on the borders of grains and dendrites.

According to the data from Table 3, the graph of element concentrations in the dendritic and interdendritic areas and the graph of element concentrations in the grains and intergranular regions were constructed (Figure 4). For clarity, linear approximations have been added and the melting temperatures of the alloy elements have been additionally added next to the elements in parentheses. Figure 4a shows the ratio of the element concentrations in the interdendritic area to the dendritic area. Figure 4b shows the ratio of the element concentrations in the grain area to the mesh area. The linear approximation on the two graphs shows an increase in the ratio of the concentration of elements in the regions

with a decrease in the melting point of the elements. Only copper had the lowest melting point with the highest alloy concentration in the mesh and interdendritic regions.

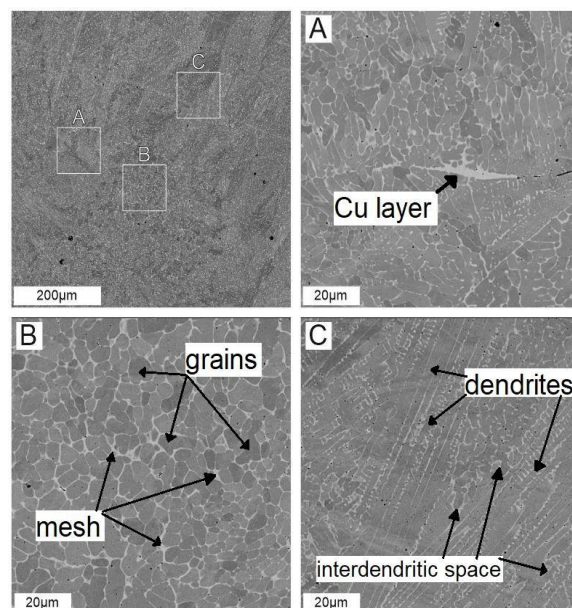


Figure 3. SEM image of microstructure of Sample No. 1 using BSE detector. Areas (A–C) are enlarged areas of the microstructure of the Sample No. 1.

Table 3. Chemical composition of different areas of Sample No. 1 in at.%.

Area	Cr	Fe	Co	Ni	Cu
A (Cu layer)	4.97	6.14	5.38	9.20	74.30
B (grains)	19.18	25.11	23.11	20.85	11.75
B (mesh)	15.24	19.53	17.04	19.64	28.56
C (dendrites)	11.43	15.76	11.33	15.56	45.92
C (interdendritic space)	6.32	7.73	6.50	11.41	68.04

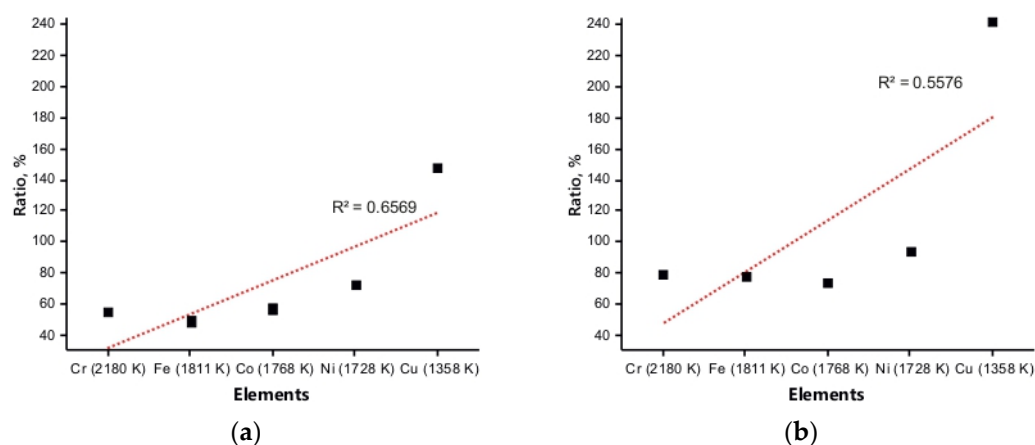


Figure 4. Graphs the ratio of the element concentrations HEA FeCoNiCrCu in different areas: (a) the interdendritic to the dendritic area; (b) the grain area to the mesh area.

Etching reveals fields with cast and grained structure in the deposited HEA FeCoNiCrCu samples. Figure 5 shows areas with different directions of dendrites (areas 1 and 2) on top of the beads and grains from the bottom of the beads in Sample No. 1. Grains are formed on top of the beads because of large heat input in these areas from previous deposited layers (Figure 5). The previous bead partially melts into a melt bath and the

powder that gets into this bath melts when the subsequent layer is deposited. Thus, the upper parts of the beads are affected by additional heat treatment. In this way, enough energy is accumulated to transform the initial dendrite structure in a granular structure as well as for increasing dendrite size [27].

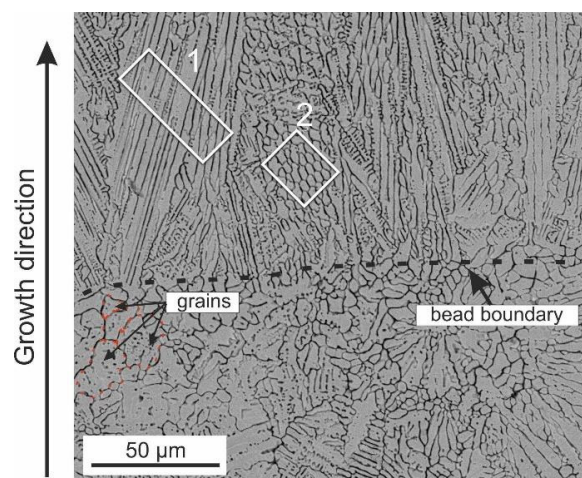


Figure 5. SEM Image of L-DED HEA Sample No. 1 using BSE detector: (1) dendrites of cast structure along the growth direction; (2) dendrites of cast structure in cross-section.

Concentration change in the range of 2–3 at.% is a normal deviation because high-entropy alloys contain more than five basic chemical elements [28]. However, Cu concentration distribution in structure is changed significantly depending on location of the FeCoNiCrCu deposited samples.

Figures 6–10 show an element mapping results for Samples No. 1–No. 5, respectively. All samples have a predominant Cu content on the crack boundary. The reason why the concentration of Cu is high on cracks' boundaries can be the lower strength of Cu-rich areas, compared with Cu-poor areas. This may cause the cracks to go through Cu-rich areas of the samples and after the crack is open, we can see Cu on its boundary. The dependence of the amount of Cu on the laser power in the samples is not observed.

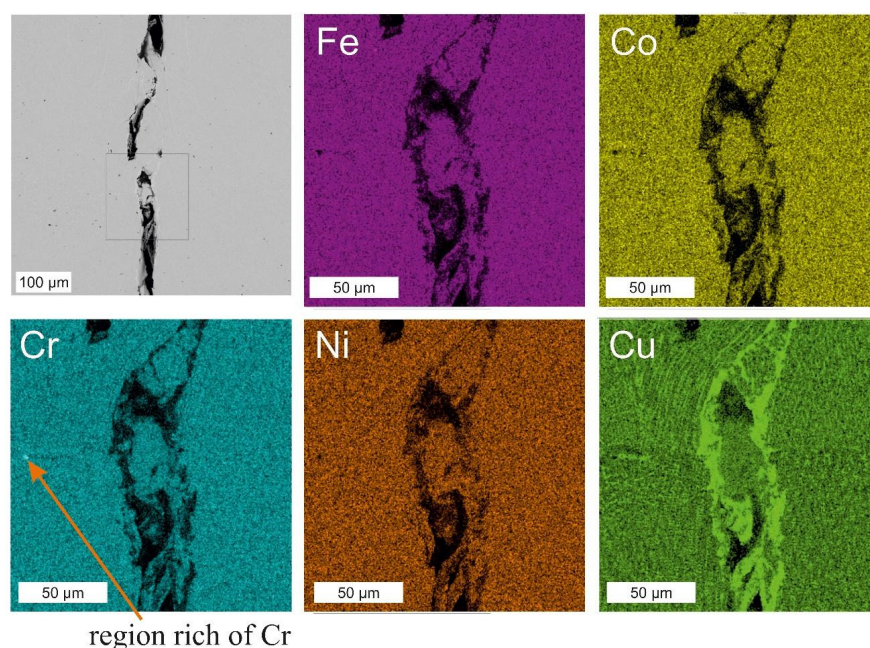


Figure 6. EDS mapping of Cr, Fe, Co, Ni, Cu elements for Sample No. 1 (1.8 kW).

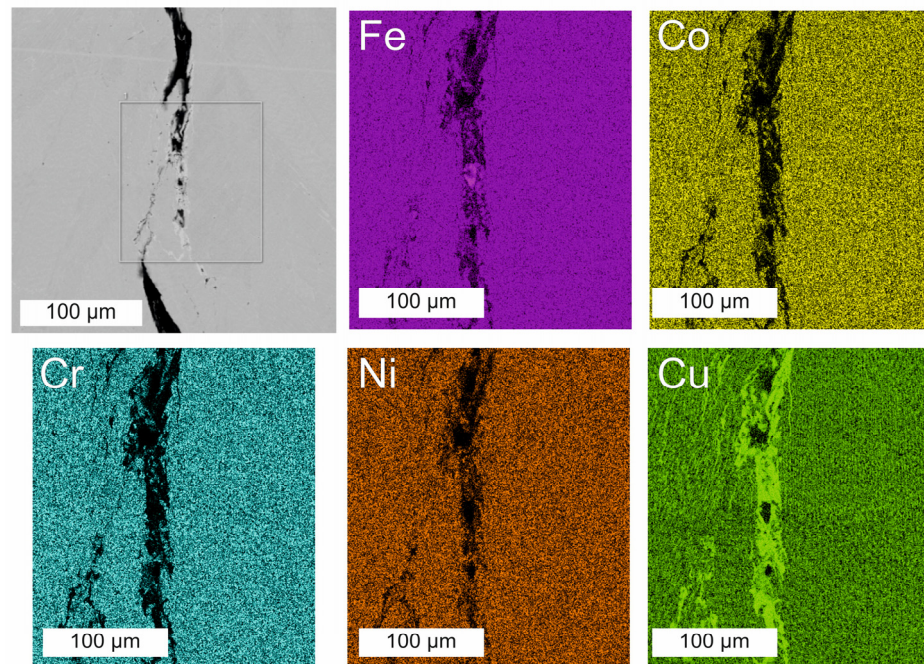


Figure 7. EDS mapping of Cr, Fe, Co, Ni, Cu elements for Sample No. 2 (2 kW).

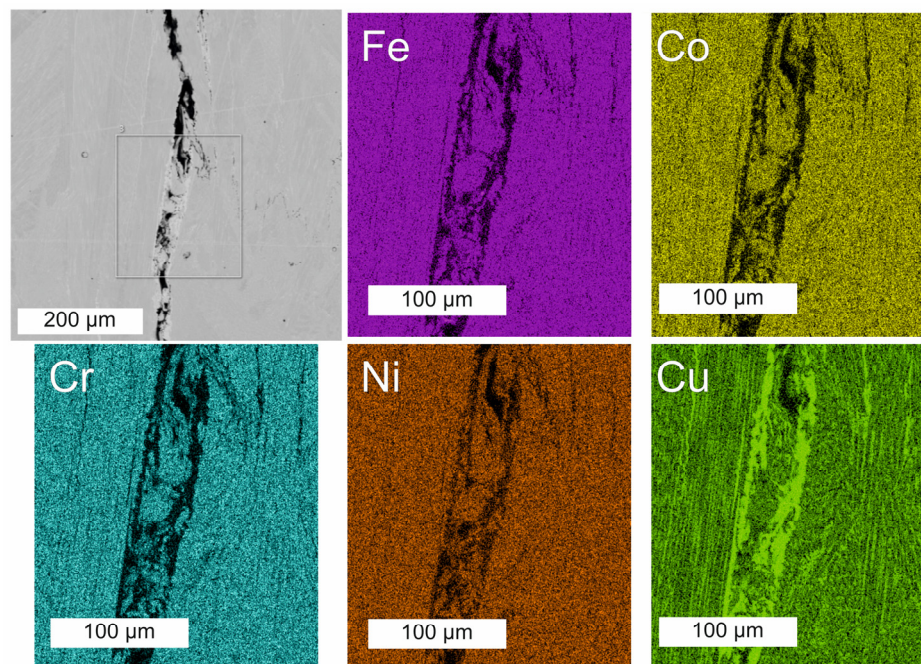


Figure 8. EDS mapping of Cr, Fe, Co, Ni, Cu elements for Sample No. 3 (2.2 kW).

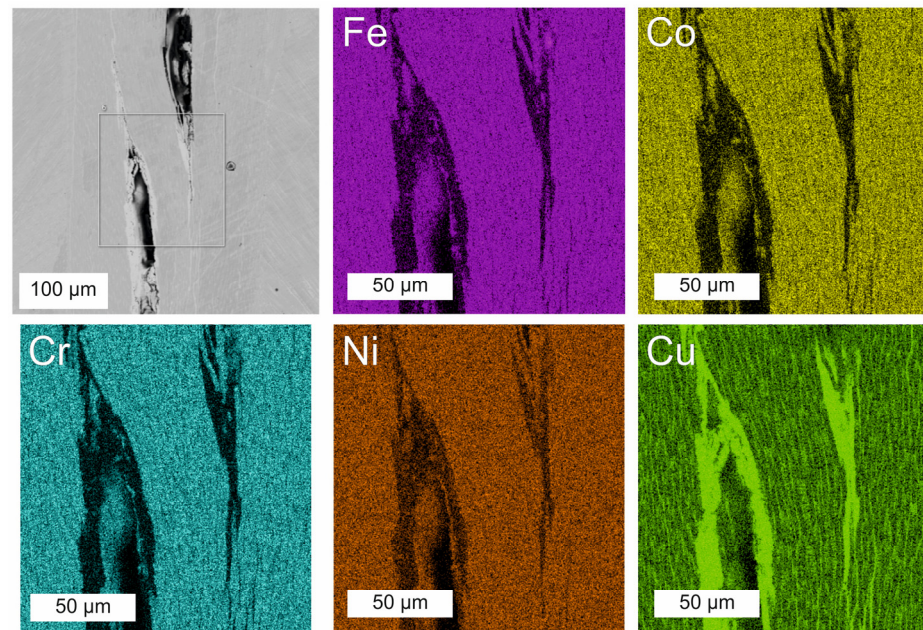


Figure 9. EDS mapping of Cr, Fe, Co, Ni, Cu elements for Sample No. 4 (2.4 kW).

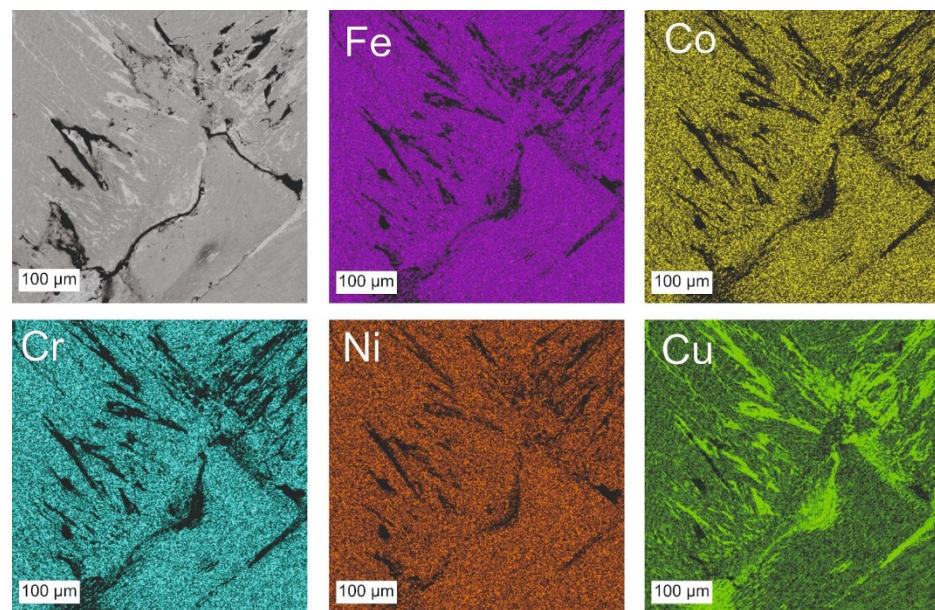


Figure 10. EDS mapping of Cr, Fe, Co, Ni, Cu elements for Sample No. 5 (2.6 kW).

Comparing HEA FeCoNiCrCu with HEA FeCoNiCrMn [25] reveals the following: in HEA FeCoNiCrCu, Ni is uniformly distributed over the entire surface but other elements can be divided into two base groups, regions rich of Fe + Co + Cr and regions rich of Cu; on the other side, the elements of HEA FeCoNiCrMn can be divided into two base groups, regions rich of Fe + Co + Cr and regions rich of Mn + Ni + Cu. In the areas of cracks in HEA FeCoNiCrMn alloys, not only Cu, which is present in small amounts in the alloy, but also Mn, can be found. Both alloys show an increased concentration of elements with the lowest melting point of the base material in the areas of the cracks.

3.3. EBSD

To determine the direction of grain growth in the HEA FeCoNiCrCu and FeCoNiCrMn samples, EBSD was used. Figure 11 shows EBSD and the inverse pole figures (IPF) images and phase composition of deposited samples.

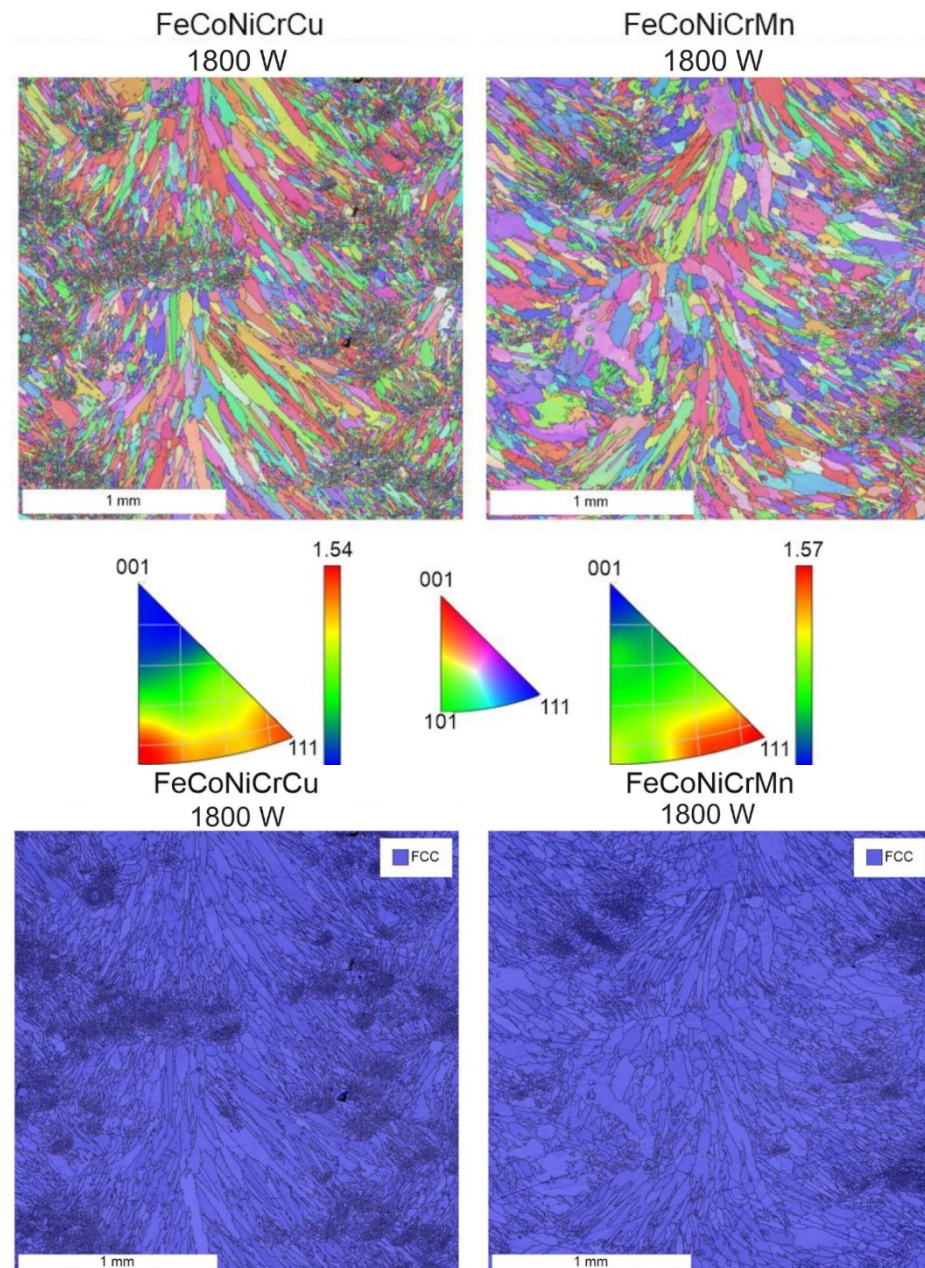


Figure 11. EBSD and IPF images of deposited samples.

In both alloys, a single-phase FCC structure is observed without any liquations. The shape of the bead with elongated dendrites growing to the top of the bead is clearly traced. In those places where beads overlap each other, we can see fine equiaxed grains, which indicate the presence of recrystallization in these places. This happens because of the additional heat input from the upper beads, as it deposits onto the already solid cooled metal of the lower beads.

These are the main directions of crystal growth in FeCoNiCrCu alloy 111 and 101, and 111 in FeCoNiCrMn alloy.

Kernel average misorientation (KAM) maps in Figure 12. The KAM value can be recognized as an indicator of dislocation density. We can observe here misorientation in the fine-grained zone. This indicates that there was a recrystallization and the angles between the initial dendrites and recrystallized grains are higher than the angles between dendrites. Those angles colored green are in Figure 12. There are also scratches shown as green. This is a typical sample preparation defect which we could not avoid.

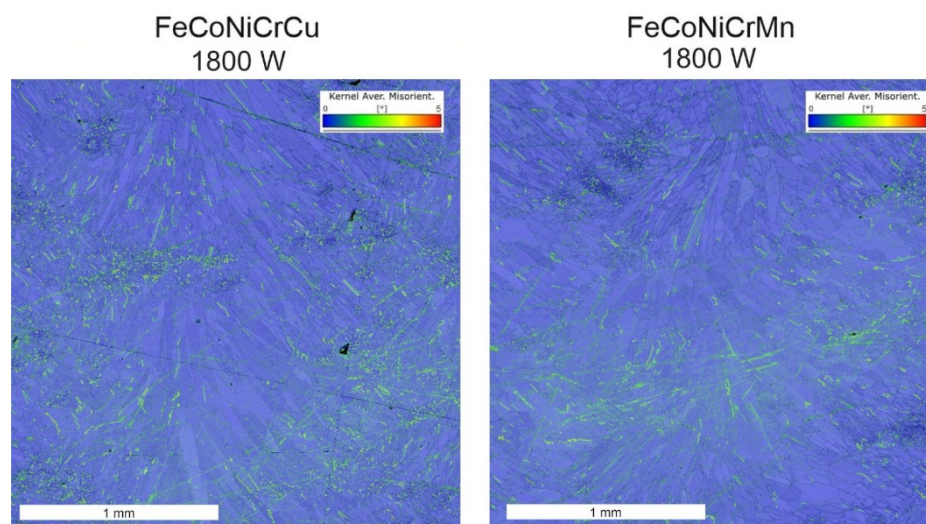


Figure 12. Kernel average misorientation (KAM) maps of the FeCoNiCrCu and FeCoNiCrMn.

Both HEA FeCoNiCrCu and HEA FeCoNiCrMn have an FCC structure. Grain growth in the HEA FeCoNiCrMn is mainly in the direction 111, and a dendritic structure with fine-grained structure is observed in the places of remelting of the beads when the next layer is surfaced. In the HEA FeCoNiCrCu with grain growth in directions 111 and 101, a dendritic structure with fine-grained structure is also observed.

Figure 13 shows the large misorientation angles in the HEA FeCoNiCrCu and FeCoNiCrMn with a maximum concentration at 45 degrees. There is also a tendency to increase the number fraction with an increase in the misorientation angle.

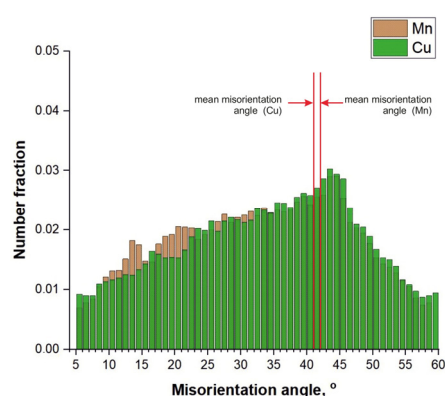


Figure 13. Histogram of the distribution of misorientation angles of the samples.

Figure 14a shows cracks in Sample No. 1. Dendrite microstructures with primary dendrite arms are observed, demonstrating the evidence of trapped liquid films. Figure 14b shows a crack after EBSD analysis. The crack going along the grain boundary and angle between grains is 40° . This observation corresponds with the histogram on Figure 13 and tells us that one of the reasons for cracking in this HEA is grain boundary misorientation.

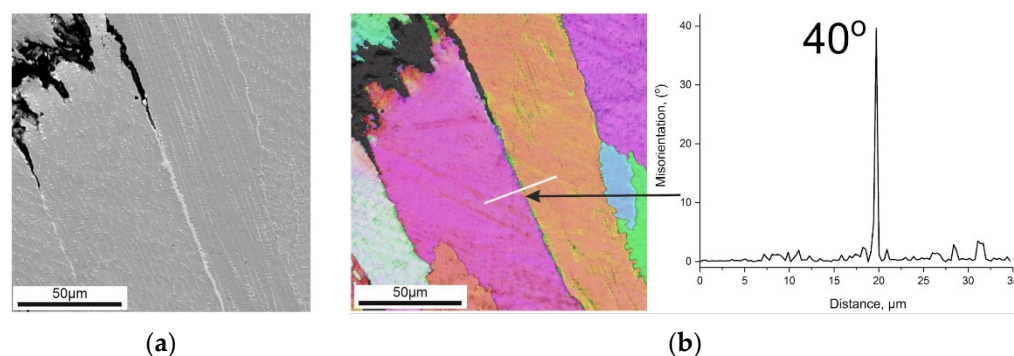


Figure 14. (a) BSE image of the crack in Sample No. 1; (b) EBSD inverse pole figure (IPF) map of the crack.

Comparing HEA FeCoNiCrCu with HEA FeCoNiCrMn [25] reveals the following: both alloys have cracks in places with a misorientation angle of up to about 45 degrees.

3.4. Microhardness

Microhardness measurements were taken to assess the mechanical properties of HEA FeCoNiCrCu. Microhardness was measured across the height of the product to determine changes in values. This was possible because of the accumulation of heat in the product as the number of bead layers increases. The degree of heat used also affected the results, so Figure 14 shows the results of microhardness measurements for Samples No. 1 and No. 5, with minimum and maximum laser powers in the study, as well as a schematic of the points used for microhardness measurement in the cross-section of the samples. FeCoNiCrMn microhardness data were also included for comparison. Figure 15 also displays the first layers of the product, which are characterized by variations in microhardness compared to the layers above them, due to mixing with the steel substrate during deposition. Elements from the substrate are present in the composition of these first layers.

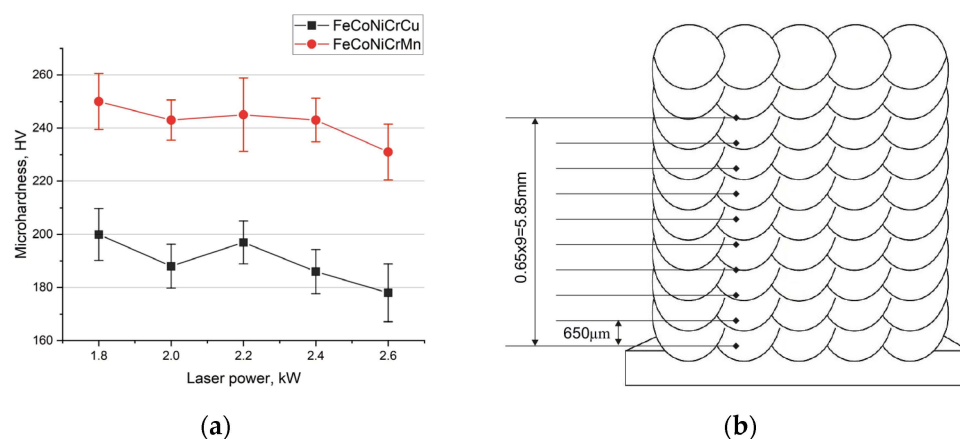


Figure 15. (a) Microhardness of samples; (b) scheme of indentations for measuring microhardness in the cross-section of the samples.

Values of microhardness of both alloys slightly decrease from 250 HV to 231 HV in the FeCoNiCrMn HEA and from 200 HV to 178 HV in the FeCoNiCrCu HEA. The deviation is about 10 HV for all samples. Also, despite the higher microhardness at a lower laser power, a lower microhardness of the first bead is noted. It can be explained by the presence of more defects in the samples with higher laser power.

Comparing HEA FeCoNiCrCu with HEA FeCoNiCrMn [25] reveals the following: the average microhardness of the FeCoNiCrCu HEA is 20% less than in the FeCoNiCrMn HEA.

3.5. XRD Analysis

X-ray diffraction was used to determine crystal structure of Samples No. 1 and No. 5 of FeCoNiCrCu HEA. Figure 16 shows the X-ray diffraction patterns for Samples No. 1 and No. 5 of FeCoNiCrCu HEA and FeCoNiCrMn HEA with minimum and maximum laser power in the study. XRD patterns tell us that FeCoNiCrCu HEA has a single-FCC solid-solution phase with a crystal lattice parameter equal to $3.57\text{\AA}$ in both the 1st and 5th Samples. The predominant direction of grains growth is the direction (111) for both FeCoNiCrCu HEA and FeCoNiCrMn HEA [25]. The difference in dominant growth direction between XRD and EBSD can be explained by the difference in scale of the taken images.

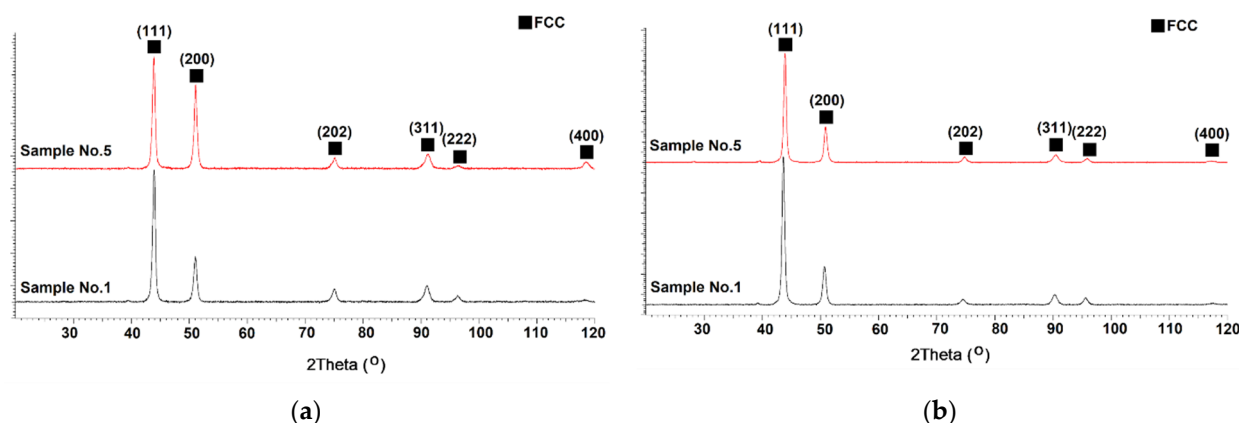


Figure 16. XRD patterns: (a) FeCoNiCrCu; (b) FeCoNiCrMn.

The FeCoNiCrMn high-entropy alloy has a similar XRD pattern with an FCC solid-solution phase [25]. The average lattice parameter is $3.57\text{\AA}$ for the 1st sample and $3.58\text{\AA}$ for the 5th one. The (200) growth direction is less dominant in FeCoNiCrMn, compared with FeCoNiCrCu.

4. Conclusions

Samples of HEA FeCoNiCrCu obtained by Laser directed energy deposition were studied and the following results were obtained:

- All samples have cracks vertically along the height;
- Fine-grained and dendrite structures were observed;
- Predominant directions of dendrite growth are (111) and (200);
- Cracks were observed at the places with large misorientation angle;
- There is a division into areas with a high content of elements Fe + Co + Cr and Cu, Ni evenly distributed. Cu-element is mainly found in cracks;
- The average microhardness of HEA FeCoNiCrCu is 240 HV.

Replacing the element Mn with Cu in HEA FeCoNiCrMn led to a shift in the dendrite growth from one to two predominant directions and a decrease in the average microhardness by 20%. The same structures and similar location of cracks were found in HEA FeCoNiCrMn. Since replacing manganese with copper leads to an increase in the number of cracks, it is recommended to reduce the copper concentration in the HEA named FeCoNiCrCu for the L-DED products to be successfully obtained.

Author Contributions: Conceptualization, E.K.; methodology, E.K.; software, E.K.; validation, E.V., O.K.-K. and M.G.; formal analysis, E.K., I.K. and S.S.; investigation, E.K. and I.K.; resources, I.K., S.S., O.K.-K. and M.G.; data curation, E.V.; writing—original draft preparation, E.K., I.K. and S.S.; 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: This laser welding and structure research was supported by the Russian Science 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. HEA synthesis was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the World-class Research Center program: Advanced Digital Technologies, contract No. 075-15-2022-312 dated 20 April 2022.

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

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

References

1. Easo, G.P.; Raabe, D.; Ritchie, R.O. High-entropy alloys. *Nat. Rev. Mater.* **2019**, *4*, 515–534. [\[CrossRef\]](#)
2. Geanta, V.; Voiculescu, I.; Milosan, I.; Istrate, B.; Mates, I.M. Chemical Composition Influence on Microhardness, Microstructure and Phase Morphology of Al_xCrFeCoNi High Entropy Alloys. *Rev. Chim.* **2018**, *69*, 798–801. [\[CrossRef\]](#)
3. Hui, Z.; Pan, Y.; He, Y.-Z. Synthesis and characterization of FeCoNiCrCu high-entropy alloy coating by laser cladding. *Mater. Des.* **2011**, *32*, 1910–1915. [\[CrossRef\]](#)
4. Sonar, T.; Ivanov, M.A.; Trofimov, E.; Tin'gaev, A.K.; Suleymanova, I. An overview of microstructure, mechanical properties and processing of high entropy alloys and its future perspectives in aeroengine applications. *Mater. Sci. Energy Technol.* **2023**, *7*, 35–60. [\[CrossRef\]](#)
5. Costas Bosque, D. Characterization of high-entropy alloys: Study of the addition of aluminum to the high entropy system HfMoTaTi+Al. *Univ. Politècnica Catalunya* **2018**, *493*, 148–153.
6. Zhang, K.; Fu, Z. Effects of annealing treatment on phase composition and microstructure of CoCrFeNiTiAl_x high-entropy alloys. *Intermetallics* **2012**, *22*, 24–32. [\[CrossRef\]](#)
7. Ren, B.; Liu, Z.X.; Li, D.M.; Shi, L.Q.; Cai, B.; Wang, M.X. Effect of elemental interaction on microstructure of CuCrFeNiMn high entropy alloy system. *J. Alloys Compd.* **2010**, *493*, 148–153. [\[CrossRef\]](#)
8. Zhang, G.; Yang, X.; Qi, W.; Li, Y.; Wang, W.; Chen, Y.; Li, J.; Li, L. Effect of Co on phase stability and mechanical behavior of Co_xCrFeNiMnAl_{0.3} high entropy alloys with micro/nano hierarchical structure. *Mater. Des.* **2022**, *215*, 110442. [\[CrossRef\]](#)
9. Shun, T.T.; Hung, W.J. Effects of Cr Content on Microstructure and Mechanical Properties of AlCoCr_xFeNi High-Entropy Alloy. *Adv. Mater. Sci. Eng.* **2018**, *2018*, 5826467. [\[CrossRef\]](#)
10. Osintsev, K.; Gromov, V.E.; Konovalov, S.; Ivanov, Y.F.; Panchenko, I. High-entropy alloys: Structure, mechanical properties, deformation mechanisms and application. *Izv. Ferr. Metall.* **2021**, *64*, 249–258. [\[CrossRef\]](#)
11. John, M.S.; Nagalakshmi, R.; Epshiba, R. High entropy alloys properties and its applications—An overview. *Eur. Chem. Bull.* **2015**, *4*, 279–284. [\[CrossRef\]](#)
12. Li, M.X.; He, Y.Z.; Sun, G.X. Laser cladding Co-based alloy/SiCp composite coatings on IF steel. *Mater. Des.* **2004**, *25*, 355–358. [\[CrossRef\]](#)
13. Zhang, H.; He, Y.Z.; Yuan, X.M.; Pan, Y. Microstructure and age characterization of Cu–15Ni–8Sn alloy coatings by laser cladding. *Appl. Surf. Sci.* **2010**, *256*, 5837–5842. [\[CrossRef\]](#)
14. Li, M.X.; He, Y.Z.; Yuan, X.M.; Zhang, S.H. Microstructure of Al₂O₃ nanocrystalline/cobalt-based alloy composite coatings by laser deposition. *Mater. Des.* **2006**, *27*, 1114–1119. [\[CrossRef\]](#)
15. Cai, Y.; Chen, Y.; Luo, Z.; Gao, F.; Li, L. Manufacturing of FeCoCrNiCu_x medium-entropy alloy coating using laser cladding technology. *Mater. Des.* **2017**, *133*, 91–108. [\[CrossRef\]](#)
16. Zhang, H.; He, Y.-Z.; Pan, Y.; Guo, S. Thermally stable laser clad CoCrCuFeNi high-entropy alloy coating with low stacking fault energy. *J. Alloys Compd.* **2014**, *600*, 210–214. [\[CrossRef\]](#)
17. Lin, C.M.; Tsai, H.-L.; Bor, H.-Y. Effect of aging treatment on microstructure and properties of high-entropy Cu_{0.5}CoCrFeNi alloy. *Intermetallics* **2010**, *18*, 1244–1250. [\[CrossRef\]](#)
18. Thangaraju, S.; Bouzy, E.; Hazotte, A. Phase stability of a mechanically alloyed CoCrCuFeNi high entropy alloy. *Adv. Eng. Mater.* **2017**, *19*, 1700095. [\[CrossRef\]](#)
19. Nagase, T.; Rack, P.D.; Noh, J.H.; Egami, T. In-situ TEM observation of structural changes in nano-crystalline CoCrCuFeNi multi-component high-entropy alloy (HEA) under fast electron irradiation by high voltage electron microscopy (HVEM). *Intermetallics* **2015**, *59*, 32–42. [\[CrossRef\]](#)

20. Huang, S.; Vida, Á.; Molnár, D.; Kádas, K.; Varga, L.K.; Holmström, E.; Vitos, L. Phase stability and magnetic behavior of FeCrCoNiGe high-entropy alloy. *Appl. Phys. Lett.* **2015**, *107*, 251906. [\[CrossRef\]](#)
21. Na, S.M.; Yoo, J.H.; Lambert, P.K.; Jones, N.J. Room-temperature ferromagnetic transitions and the temperature dependence of magnetic behaviors in FeCoNiCr-based high-entropy alloys. *AIP Adv.* **2018**, *8*, 056412. [\[CrossRef\]](#)
22. Zuo, T.; Gao, M.C.; Ouyang, L.; Yang, X.; Cheng, Y.; Feng, R.; Chen, S.; Liaw, P.K.; Hawk, J.A.; Zhang, Y. Tailoring magnetic behavior of CoFeMnNiX (X= Al, Cr, Ga, and Sn) high entropy alloys by metal doping. *Acta Mater.* **2017**, *130*, 10–18. [\[CrossRef\]](#)
23. Huang, E.W.; Chou, H.S.; Tu, K.N.; Hung, W.S.; Lam, T.N.; Tsai, C.W.; Chiang, C.-Y.; Lin, B.-H.; Yeh, A.-C.; Chang, S.-H.; et al. Element effects on high-entropy alloy vacancy and heterogeneous lattice distortion subjected to quasi-equilibrium heating. *Sci. Rep.* **2019**, *9*, 14788. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Chen, X.; Ivanov, Y.F.; Gromov, V.E.; Efimov, M.O.; Konovalov, S.V.; Shlyarov, V.V.; Panchenko, I.A. High-Entropy FeCoCrNiMn and FeCoNiCrAl Alloys Coatings: Structure and Properties. *Proc. Altai State Univ. (Izv. Altayskogo Gos. Univ.)* **2023**, *4*, 11–19. [\[CrossRef\]](#)
25. 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. [\[CrossRef\]](#)
26. Vildanov, A.M.; Babkin, K.D.; Alekseeva, E.V. Macro defects in direct laser deposition process. *Mater. Today Proc.* **2020**, *30*, 523–527. [\[CrossRef\]](#)
27. Lu, Y.; Wang, J.; Williams, S.; Zhu, L.; Ding, J.; Diao, C.; Jiang, Z. Additive manufacturing of a functionally graded high entropy alloy using a hybrid powder-bed wire-based direct energy deposition approach. *Addit. Manuf.* **2023**, *63*, 103424. [\[CrossRef\]](#)
28. Vander Voort, G.F.; Lampman, S.R.; Sanders, B.R.; Anton, G.J.; Polakowski, C.; Kinson, J.; Scott, W.W., Jr. *ASM Handbook Volume 9: Metallography and Microstructures*; ASM International: Materials Park, OH, USA, 2004.

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.