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Article

Microstructure and Properties of Additively Manufactured AlCoCr_{0.75}Cu_{0.5}FeNi Multicomponent Alloy: Controlling Magnetic Properties by Laser Powder Bed Fusion via Spinodal Decomposition



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Abstract: A non-equiatomic AlCoCr_{0.75}Cu_{0.5}FeNi alloy has been identified as a potential high strength alloy, whose microstructure and consequently properties can be widely varied. In this research, the phase structure, hardness, and magnetic properties of AlCoCr_{0.75}Cu_{0.5}FeNi alloy fabricated by laser powder bed fusion (LPBF) are investigated. The results demonstrate that laser power, scanning speed, and volumetric energy density (VED) contribute to different aspects in the formation of microstructure thus introducing alterations in the properties. Despite the different input parameters studied, all the as-built specimens exhibit the body-centered cubic (BCC) phase structure, with the homogeneous elemental distribution at the micron scale. A microhardness of up to 604.6 ± 6.8 HV0.05 is achieved owing to the rapidly solidified microstructure. Soft magnetic behavior is determined in all as-printed samples. The saturation magnetization (M_s) is dependent on the degree of spinodal decomposition, i.e., the higher degree of decomposition into A2 and B2 structure results in a larger M_s . The results introduce the possibility to control the degree of spinodal decomposition potentiality of LPBF could benefit the development of new functional materials.

Keywords: high-entropy alloys; laser powder bed fusion; selective laser melting; direct metal laser sintering; spinodal decomposition; magnetic properties

1. Introduction

Multicomponent alloys, including high-entropy alloys (HEAs), represent the fastest growing area of innovations of metallic materials since the last decade. HEAs represent not only an interesting field in materials with the diverse possibility to explore, but most importantly, the promising improvements with properties, such as, e.g., strength and ductility [1], oxidation and wear resistance [2], corrosion resistance [3], and irradiation resistance [4,5]. The concept of mixing multiple principal elements, equiatomic, or near-equiatomic compositions, in one alloy system, and resulting in the high configurational entropy to promote the solid solution, was initially materialized by Cantor et al. [6] and Yeh



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Copyright: © 2022 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/). et al. [7]. Among varieties of HEA systems, Al_x CoCrCuFeNi (x = 0-3, in molar ratio) has been studied by Yeh et al. [7] as an example that only simple solid solution structures form in HEAs, instead of the mixture of complicated phases produced in conventional alloys containing multiple principal elements. It has been confirmed that the $Al_xCoCrCuFeNi$ alloy consists of a single face-centered cubic (FCC) structure when the aluminum content x was in the range of 0 to 0.5 (equivalent to 0 to 9.09 at%), while a combination of FCC and body-centered cubic (BCC) structure was formed at x = 0.8. When x was increased further, the modulated phase structures were formed until a single BCC phase structure was achieved when x > 2.8 (equivalent to 35.90 at%). Apart from the microstructural evolution, the addition of aluminum in HEAs is also found to lower the density and enhance the strength as well as the oxidation resistance [8]. Therefore, AlCoCrCuFeNibased alloys have attracted interest widely and have become one of the most studied alloy systems in HEAs [9–11]. To date, HEAs are mainly fabricated by arc-melting and casting, and usually with post-treatments. Furthermore, to form a single-phase structure using conventional methods, the Al content needs to be kept either quite low (below 9.09 at%) or high (above 35.90 at%). Consequently, the majority of AlCoCrCuFeNi based alloys produced conventionally display the duplex structures composed of BCC and FCC phases [12,13]. The complexity of microstructure also arises from the segregation of copper, which is presented in the AlCoCrCuFeNi based alloys [12,13]. One strategy is to reduce the content of copper. Tung et al. [12] found that a single BCC crystal phase was achieved in the as-cast AlCoCrCu_{0.5}FeNi alloy, and the segregation of copper, as well as the formation of interdendrites, was suppressed significantly. On the other hand, it is reported that the single BCC phase structure has been detected in the equiatomic AlCoCrCuFeNi alloy after splat quenching or ultrarapid quenching, which involves the rapid solidification process [13,14]. However, due to the complex nature of multicomponent alloys, their fabrications challenge the controllability of techniques and the processing cost.

Laser powder bed fusion (LPBF) technique, also known as selective laser melting (SLM), is one of the most suitable additive manufacturing (AM) methods to perform the fabrication of multicomponent alloys. It exhibits high-level local controllability, high resolution and accuracy, and the capability of producing refined microstructure with superior properties owing to the rapid solidification process [15]. It exhibits the advantage of building a broad range of metal materials with complicated shapes using laser beam layer by layer, with various optional possibilities for post processing [16]. The first additively manufactured multicomponent alloy has been reported by Brif et al. [17], who fabricated FeCoCrNi alloy employing LPBF. Their results revealed promising mechanical properties comparable to conventional stainless steels, benefiting from the refinement of microstructure through the LPBF process. Some studies have investigated the printability of various AlCoCrFeNi based HEAs, including Al_xCoCrFeNi [18,19], AlCoCrCuFeNi [20], AlCoCrFeMnNi [21], and AlCoCrFeNiTi_{0.5} [22]. These studies have shown that LPBF produces hierarchical microstructures, including cellular structure, modulation, and dislocation cells, which are beneficial to the advancement of mechanical properties. To date, the research concerning LPBF-built AlCoCrCuFeNi alloy remains scarce. As mentioned above, Singh et al. [13] produced an equiatomic AlCoCrCuFeNi alloy consisting of a single BCC phase by splat quenching from the melt. On the other hand, Wang et al. [20] found that the LPBF-processed equimolar AlCoCrCuFeNi alloy consists of mixed BCC and FCC phase structure with FCC content up to 40.20%. Splat quenching introduces a cooling rate of 10^6-10^7 K/s [13], which is similar to that in the LPBF process [23,24]. This indicates that it is crucial to optimize the process parameters in LPBF and understand the rapidly solidified microstructure, as well as its relation to properties. Such knowledge could assist the development of novel multicomponent alloys.

While the focus of multicomponent alloys research is primarily on their mechanical properties, the functional properties, such as magnetic properties, also attract interest with the promising potentials to be explored [25–27]. Zhang et al. [28] found that the as-cast equiatomic AlCoCrCuFeNi alloy, which consisted of a mixture of FCC and BCC phase,

exhibited saturation magnetization of 38.18 Am²/kg at ambient temperature, which is as good as for the soft ferrite materials. The phase formation of AlCoCrCuFeNi based alloys in relation to the spinodal decomposition has been described by Singh et al. [13], Zhang et al. [29], and Peter et al. [30], as summarized in Table 1. The splat-quenched equiatomic AlCoCrCuFeNi alloy, which experienced a cooling rate of 10^{6} – 10^{7} K/s, showed a single BCC phase structure [13]. The moderate cooling rate of 10^3 – 10^4 K in the gasatomized AlCoCr_{0.75}Cu_{0.5}FeNi powder resulted in a phase separation from solid solution into Al-Ni-rich BCC B2 structure, Fe-Cr-rich BCC A2 structure, and Cu precipitates in the nanoscale, and it was proposed that the formation of A2 structure would be suppressed by the higher cooling rate [30]. Al-Ni-rich ordered BCC phase was associated with the weakened ferromagnetism [25,31]. As the cooling rate was decreased to 10^2 - 10^3 K/s, the formation of dendritic and interdendritic features was observed at the sub-micron scale in the spray-cast sample [29]. The dendrites contained Al-Ni-rich and Fe-Cr-rich structures along with Cu-rich precipitates, and the interdendrites corresponded to Cu-rich precipitates [29]. Finally, when a cooling rate of 10–20 K/s typical for casting was employed, a complicated mixture of dendrites and interdendrites consisting of several types of BCC and FCC phase structures were observed [13]. The saturation magnetization was thereby dependent on the degree of decomposition of Cr-Fe-Co-rich phase (that existed in the dendrites) into the ferromagnetic Fe-Co-rich phase and antiferromagnetic Cr enriched phase, i.e., the higher the degree of decomposition under the slower cooling rate, the higher the reached saturation magnetization was. As a result, the as-cast sample possessed a higher saturation magnetization of 46 Am²/kg at 14 T and 300 K than the splat-quenched one [32]. These observations show that apart from solid solution, the spinodal decomposition is capable of improving the properties of multicomponent alloys such as magnetic properties. Such enhancement of magnetic properties by spinodal decomposition has been recently materialized by Rao et al. [33]. More importantly, according to the phase evolution stated in [13,29,30], the spinodal decomposition in the AlCoCrCuFeNi based alloy is governed by the cooling rate. This suggests that in combination with one of the advantages of LPBF, namely, controlling the cooling rate by varying the process parameters, it is feasible to govern the formation of microstructure and consequently achieve desired magnetic properties by altering the process parameters, without the need for post treatments or changing the chemical compositions of the raw powder.

Table 1. Phase formation in correlation to fabrication method and cooling rate in AlCoCrCuFeNi based alloys.

Alloy	Method	Cooing Rate (K/s)	Phase Structure	Ref.
AlCoCrCuFeNi	Splat quenching	$10^{6} - 10^{7}$	BCC	[13]
AlCoCr _{0.75} Cu _{0.5} FeNi	Gas atomization	$10^3 - 10^4$	BCC A2 + BCC B2 + Cu precipitates	[30]
			Dendrites: Al-Ni-rich and Fe-Cr-rich	
AlCoCrCuFeNi	Spray casting	$10^2 - 10^3$	structures, with Cu-rich precipitates.	[29]
			Interdendrites: Cu-rich precipitates.	
			Dendrites: Al-Ni-rich, Cr-Fe-rich,	
AlCoCrCuFeNi	Casting	10-20	Al-Ni-Fe-rich, and Cu-rich precipitates.	[13]
			Interdendrites: Cu-rich.	

The detailed microstructure of the gas-atomized AlCoCr_{0.75}Cu_{0.5}FeNi powder used in this research has been reported in [30,34]. This multicomponent alloy has not been fabricated by LPBF before, and the knowledge of its microstructure and properties remains inadequate. Further research is essential to evaluate especially the magnetic properties in relation to the spinodal decomposition of LPBF-built multicomponent alloys, which have been scarcely examined previously. In this study, the feasibility of additive manufacturing of AlCoCr_{0.75}Cu_{0.5}FeNi alloy composed of a single-phase structure and the controllability of the degree of spinodal decomposition are explored. The influence of process parameters in the LPBF process on microstructure, mechanical and magnetic properties is determined.

2. Materials and Methods

2.1. Specimens Preparation

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The powder AlCoCr0.75Cu0.5FeNi was atomized with nitrogen using a free-fall ato izer in a spray forming process (ID number Sk2-800, more details as reported in [30,34 Compared to equimolar AlCoCrCuFeNi alloy, the content of Cu is reduced in order avoid segregation caused by its positive mixing enthalpy with each element of Cr, Co, 2 and Fe Marrials and Methods

The partiticle class size of the raw powder used was in the range of 20–63 μm. Spe mens were additively maturated by with a process (ID number Sk2-800, more details as reported in [30,34]). terbium fiber date in a spray forming process (ID number Sk2-800, more details as reported in [30,34]). The hatthespace of the quincilla Allow reasonance of the quince of the specific of the quince of th

the scanning speed. The resulting variations $\mu_D V \underline{E} \underline{D}$ are obtained according to [35] as:

 $\int v \cdot h \cdot t$

where *P* is laser power, *v* is scanning speed, h_{i} is the hatch spacing, and *t* is the layer thin ness. Processing of the second set of samples (specimens #3–5) was carried out applying the same power, *v* is scanning speed, *h* is the hatch spacing, and *t* is the layer thickness. The same power, *v* is scanning speed, *h* is the hatch spacing, and *t* is the layer thickness. The same power by is laser power, *v* is scanning speed, *h* is the hatch spacing, and *t* is the layer thickness. The same power by is laser power, *v* is scanning speed, *h* is the hatch spacing, and *t* is the layer thickness. The same power by the same power by the same power by the second set of states power and the space of the same set power of the space of the



Figure 1. (a) Schematic illustration of LPBF scanning strategy, and (b) as-built AlCoCr_{0.75}Cu_{0.5}FeNi specimens applying different process parameters.

Sample #	Power (W)	Scanning Speed (mm/s)	VED (J/mm ³)
1	200	1200	92.59
2	200	1500	74.07
3	200	2000	55.56
4	180	1800	55.56
5	160	1600	55.56

Table 2. Process parameters of the LPBF-built AlCoCr_{0.75}Cu_{0.5}FeNi specimens.

2.2. Characterization Methods

The as-built specimens were initially ground with fine SiC papers down to P2500. The chemical composition was determined by the PANalytical Axios^{mAX} 3 kW wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (PANalytical, Almelo, The Netherlands). The phase structure was identified by the PANalytical X'Pert PRO MPD diffractometer applying Co-K_{α} radiation operating at 40 kV and 40 mA, with a step size of 0.0131° and a counting time of 119.85 s per step. The phase quantification was carried out on the X-ray diffraction (XRD) pattern employing the Rietveld refinement method by X'Pert HighScore Plus software (version 4.8). The theoretical density of each specimen was calculated based on XRD patterns. The density and relative density were estimated by the Archimedes principle. The electrochemical etching was performed with the 13 vol.% HNO₃-ethanol solution at -23 °C under 8 V. The microstructure of the specimens was studied by the JEOL JIB-4700F (JEOL, Tokyo, Japan) focused-ion-beam scanning electron microscope (FIB-SEM) equipped with a JEOL JED-2300 Analysis Station Plus energy-dispersive X-ray spectrometer (EDS) system. The preparation of EBSD specimens was performed using the Buehler VibroMet 2 vibratory polisher (Buehler, Lake Bluff, IL, USA) with Al_2O_3 suspension with a particle size of 0.05 µm for 18 h. The crystal orientation was characterized by the Zeiss Ultra 55 field-emission scanning electron microscope (FE-SEM) (Zeiss, Oberkochen, Germany) equipped with an Oxford Instruments Nordlys F⁺ electron backscatter diffraction (EBSD) camera. A step size of 1 µm was employed. Grain structure was determined using fast multiscale clustering (FMC) [36] using the following values: C_{Maha} of 1, C_{Maha0} of 5, gammaW of 25, alpha of 0.2, and beta of 0.3. Grain size was estimated using grain boundary images obtained through FMC analysis and calculated using the method outlined by Lehto et al. [37]. The microhardness was examined by the Innovatest Nexus 4303 Vickers hardness tester according to ISO 6507-1:2018 [38], at a force of 0.4903 N and a dwell time of 10 s. Ten points were measured for each specimen.

Magnetic properties were evaluated using a vibrating sample magnetometer (VSM) installed in the Quantum Design Physical Property Measurement System (PPMS) (Quantum Design, Inc., San Diego, CA, USA). The thermomagnetic curves, i.e., magnetization versus temperature curves, were measured in low (0.01 T) and saturation (2 T) fields in the temperature interval of 10 to 800 K in an attempt to estimate the ferromagnetic Curie point. Furthermore, the magnetic behavior of one specimen was determined in 2 T field at a temperature from 305 to 1000 K. Saturation magnetization M_s from magnetization loops was measured up to 9 T field at 10 K and 300 K. To determine magnetic coercivity, the additional measurement of magnetization loops at room temperature was performed using VSM PAR (Quantum Design, Inc., San Diego, CA, USA) with an electromagnet.

3. Results

3.1. Density and Chemical Composition

The effect of process parameters on Archimedes density (AD) and relative density (RD) of LPBF-built AlCoCr_{0.75}Cu_{0.5}FeNi alloy is depicted in Figure 2. As shown in Figure 2a, the maximum AD of 7.070 \pm 0.017 g/cm³ and RD of approximately 97% are achieved with the highest applied VED of 92.59 J/mm³. When the input VED is reduced from 92.59 to 55.56 J/mm³, corresponding to an increase of the scanning speed from 1200 to 2000 mm/s at a laser power of 200 W, AD and RD slightly fluctuate to 7.041 \pm 0.023 g/cm³ and 96.7% \pm 0.3%, respectively. On the other hand, in Figure 2b, both AD and RD in-

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with the highest applied VED of 92.59 J/mm³. When the input VED is reduced from 92.59 to 55.56 J/mm³, corresponding to an increase of the scanning speed from 1200 to 2000⁴ mm/s at a laser power of 200 W, AD and RD slightly fluctuate to 7.041 ± 0.023 g/cm³ and 96.7% ± 0.3%, respectively. On the other hand, in Figure 2b, both AD and RD increase noticeably from 6.898 ± 0.014 ± 0.023 g/cm³ and 94.5% ± 0.7.041 ± 0.023 g/cm³ at the same applied VED of 55.56 J/mm⁵. In this case, the laser power and scanning speed are increased from 160 W and 1600 mm/s to 200 W and in 2000 mm/s, respectively.



Figliger 2.2 ADDand IRD of asprinted AKICOG. 19 55 Constants Nipspirotemepsoppodd cordien (d) eth (a) athe same last as provered b200W with different scanning speed shah (b) (b) ethansa MED/001556655.5601/mm³.

The secondary electron (SE) images on both theix y and XT plane of each specimen are shown in Figure 3a. Three types of defects are found responsible for the porosity of the as-built specimens, namely, cracks, gas pores, and lack-of-fusion defects. Pores with a relatively small size and meary prefical stap one is and lack-of-fusion defects. Pores with a relatively small size and meary prefical stap one is and lack-of-fusion defects. Pores with a relatively small size and meary prefical stap one is and lack-of-fusion defects. Pores with a relatively small size and pear spherical stap one is and lack-of-fusion defects. Pores with a relatively small size and pear spherical stap one is an one of the associated provided the state of the astrony of the speciment is the speciment of the period of the period of the period relatively small size and pear spherical shape are provided to be provided to the period of the speciment of the period of the speciment of the speciment of the speciment of the period full of the speciment of the period of the period of the period of the period full of the period full of the period full of the period full of the period of the period

changes most considerably. Comparing to the powder composition reported in [30], the composition of the reference PECS sample remains identical, while the Al content in LPBFbuilt specimens declines to a varying degree. This is expected, as the Al element has the lowest boiling point and heat of evaporation of the elements involved [40]. Cu content also decreases somewhat but not as clearly, whilst the content of the other four alloying elements correspondingly increases slightly. When different scanning speeds are applied at a laser power of 200 W, the element content of specimens alters only within the uncertainty of measurements despite different VEDs. Under the same VED input of 55.56 J/mm³, adjusted with the laser power and the scanning speed, the average content of the specimens remains roughly the same, taking into account the measurement errors. Only the average Al content appears to change slightly with changing laser power and the scanning speed. This suggests that the process parameters employed in this research reduce the Al content only marginally as neither the alteration of VED nor laser power or scanning speed affect the chemical composition of the specimens markedly.



Fightgene 3. SEmicrographs of as-printed AdCoCr_275Cu_5FeW specimens. (a) Images on the xy- and xz-planes. Setails of b) seas pores and (c) lack off-this on decision of the xz-plane.

The chemical composition of as-built specimens and a reference PECS sample is presented in Table 3. It is found that among all six elements, the average content of Al changes most considerably. Comparing to the powder composition reported in [30], the composition of the reference PECS sample remains identical, while the Al content in LPBF-built specimens declines to a varying degree. This is expected, as the Al element has the lowest boiling point and heat of evaporation of the elements involved [40]. Cu content also de-

Commute	Element (at%)					
Sample	Al	Cu	Fe	Ni	Со	Cr
Powder [30]	19.5	9.57	18.8	19.5	19.6	12.9
$VED = 92.59 \text{ J/mm}^3$ (P = 200 W, v = 1200 mm/s)	17.8 ± 0.12	9.3 ± 0.01	19.2 ± 0.09	20.1 ± 0.05	20.5 ± 0.04	13.1 ± 0.03
VED = 74.07 J/mm^3 (P = 200 W, v = 1500 mm/s)	17.8 ± 0.35	9.3 ± 0.02	19.2 ± 0.13	20.0 ± 0.08	20.5 ± 0.10	13.2 ± 0.08
VED = 55.56 J/mm^3 (P = 200 W, v = 2000 mm/s)	18.1 ± 0.10	9.4 ± 0.02	19.1 ± 0.03	19.8 ± 0.07	20.3 ± 0.02	13.3 ± 0.03
VED = 55.56 J/mm^3 (P = 180 W , v = 1800 mm/s)	17.7 ± 0.30	9.5 ± 0.05	19.1 ± 0.08	20.0 ± 0.07	20.4 ± 0.07	13.3 ± 0.08
VED = 55.56 J/mm^3 (P = 160 W , v = 1600 mm/s)	17.6 ± 0.26	9.5 ± 0.02	19.2 ± 0.04	20.0 ± 0.10	20.4 ± 0.13	13.3 ± 0.06
PECS sample	19.3 ± 0.15	9.6 ± 0.09	18.7 ± 0.07	19.6 ± 0.06	19.9 ± 0.09	12.9 ± 0.08

Table 3. Chemical composition of as-built specimens, a reference PECS sample, and the starting powder.

3.2. Phase and Microstructure

Figure 4 illustrates the XRD diffraction pattern along with the Rietveld analysis of the starting powder with the particle class size of 20–63 μ m. The 100 peak at 2 θ = 36.28° refers to the super-lattice B2 structure. A mixture of two types of BCC phase is identified, namely, the ordered B2 phase and the disordered A2 phase. According to the phase quantification analysis carried out using the Rietveld refinement method, the lattice constant of A2 structure is estimated to be $a_{A2} = 2.8732$ Å, and that of B2 structure $a_{B2} = 2.8744$ Å. The weight fractions of A2 and B2 phase are determined to be 35.8 wt% and 64.2 wt%, respectively. These results are consistent with the observations characterized by the scanning transmission electron microscopy and atom probe tomography in [30]. It is worth mentioning that in both the previous XRD analyses on the same raw powder in [30,34],

only one type of BCC phase was revealed. This is likely to result from the program settings Materials 2022, 15, x FOR PEER REV 9 of 25 of XRD measurement, e.g., the step size and count time per step, which are not efficient

enough to depict the differences of structures.



Figure 4. XRD experimental and refire time the new very boot ligit of iginal epowder.

As elongated grains are formed on the xz-plane (see in Figure 3b,c), XRD analysis has been performed on both the xy- and xz-plane of each LPBF specimen, as displayed ir Figure 5. It is noticed in Figure 5a,b that only BCC phases are detected in the LPBF specimens. On the other hand, the reference PECS sample consists of both FCC and BCC

in Figure 5. It is noticed in Figure 5a,b that only BCC phases are detected in the LPBF specimens. On the other hand, the reference PECS sample consists of both FCC and BCC phases. The weight fractions of FCC and BCC phases estimated by Rietveld refinement are 44.9 wt% and 55.1 wt%, respectively (see in Figure S1). According to Figure 5a, the intensity of the 100 and 200 diffraction peak on the xy-plane of the sample produced with the highest VED of 92.59 J/mm³ is enhanced in comparison with the raw powder, suggesting the presence of the preferred crystallographic texture, {100} plane is perpendicular to building direction. With the decrease of applied VED, the preferred orientation on the xy-plane gradually weakens. Under the same constant VED input of 55.56 J/mm³, few significant differences on the xy-plane are delineated, regardless of the alteration of both laser power and scanning speed. In addition, it is noticed that the superlattice reflection 100 is more profound on the xy-plane of samples produced by the VEDs of 92.59 and 74.07 J/mm³. On the xz-plane, XRD patterns of LPBF specimens appear similar to that of the starting bowder, as can be seen in Figure 5b, and the differences of relative intensity on the xz-plane



among each LPBF specimen are indistinguishable.

Figure 3. XRDpotteronatof as iptichted A Co Co Witten is specific presenting and a second a s (b) xz-plane, magnified 20 of 110 peak on (c) xy-plane and (d) xz-plane (b) xz-plane, magnified 20 of 110 peak on (c) xy-plane and (d) xz-plane.

The EBSD analyses of inverse pole figure (IPF) maps on the xy-plane of LPBF-built AlCoCr0.75Cu0.5FeNi specimens are illustrated in Figure 6. All the specimens display the polygonal equiaxed grains on the xy-plane, and only BCC structure has been identified. The grain size of each specimen is shown on the left corner of each map. The finest grain size of ~9.47 µm is produced when the scanning speed reaches the highest value of 2000 As shown in Figure 5c, the magnification of 2θ in the range of $51-54^{\circ}$ illustrates that the 110 peaks on the xy-plane of LPBF specimens shift to a higher angle than that of the powder, which suggests that the interplanar spacing on the xy-plane of each LPBF specimen is decreased from that of starting powder. The peak on the xy-plane detected in the sample built with the largest VED of 92.59 J/mm³ is shifted the most. As the VED declines concomitantly with the increasing scanning speed, the degree of shift of 110 peak on the xy-plane decreases, implying that the rapid solidification-induced stress concentrations on the xy-plane are increased when the scanning speed is faster. Peaks on the xy-plane are identical at a constant VED of 55.56 J/mm³, suggesting that the residual stresses on the xy-plane are similar under the same VED despite the alteration in laser power and scanning speed. The magnified 2θ range from 51° to 54° in Figure 5d illustrates a smaller degree of shift but broader 110 peaks on the xz-plane when compared with the xy-plane. The broadening of XRD peaks on the xz-plane is somewhat greater than that on the xy-plane, which is likely due to the non-symmetrical cell structure and texture.

The EBSD analyses of inverse pole figure (IPF) maps on the xy-plane of LPBF-built AlCoCr_{0.75}Cu_{0.5}FeNi specimens are illustrated in Figure 6. All the specimens display the polygonal equiaxed grains on the xy-plane, and only BCC structure has been identified. The grain size of each specimen is shown on the left corner of each map. The finest grain size of ~9.47 μ m is produced when the scanning speed reaches the highest value of 2000 mm/s

Materials 2022, 15, x FOR PEER REVIEWinder the laser power of 200 W, indicating that grain size increases with the decreasing ²⁵ applied scanning speed when the same laser power is employed.



Figure 6. EBSD IPF maps on the xy-plane of AlCoCr_{0.75}Cu_{0.5}FeNi specimens produced by the differ- **Hydre 6.** EBSD IPF maps on the xy-plane of AlCoCr_{0.75}Cu_{0.5}FeNi specimens produced by the ent process parameters. different process parameters.

The EBSD IPF maps, band contrast images with grain boundary maps, and Kernel average misorientation (KAM) maps on the xz-plane of LPBF-built AlCoCr_{0.75}Cu_{0.5}FeNi specimens are depicted in Figure 7. The IPF maps displayed in Figure 7a-1,b-1,c-1,d-1 manifest that instead of the equiaxial grains determined on the xy-plane, the grains on the

The EBSD IPF maps, band contrast images with grain boundary maps, and Kernel average misorientation (KAM) maps on the xz-plane of LPBF-built AlCoCr_{0.75}Cu_{0.5}FeNi specimens are depicted in Figure 7. The IPF maps displayed in Figure 7a-1,b-1,c-1,d-1 manifest that instead of the equiaxial grains determined on the xy-plane, the grains on the xz-plane are elongated towards the building direction, indicating that epitaxial growth occurs [41]. The average grain size of specimens estimated on the xz-plane is, therefore, larger than that determined from the xy-plane. Both the length and width of the grains reduce with the rising scanning speed; this observation is in agreement with former research, where a columnar-to-equiaxed transition (CET) of grains occurs when employing a higher cooling rate in LPBF process, and is related to the high probability of the heterogeneous nucleation under the large undercooling [42]. Merely BCC phase has also been revealed on xy-plane. The band contrast images with high angle grain boundary (HAGB, blue lines) maps and low angle grain boundary (LAGB, 5–15°, red lines) maps in Figure 7a-2,b-2,c-2,d-2 delineate the variation of the HAGBs fraction in LPBF specimens (the fraction value is shown on the upper right corner of each image). When the VED input decreases from 92.59 to 55.56 J/mm³, the fraction of HAGBs increases from ~45% to ~57%. It demonstrates that the specimen produced with the maximum VED contains the smallest proportion of HAGBs, as a consequence of the lower scanning speed employed. When applying the same VED of 55.56 J/mm³ with applied laser power of 180 W and scanning speed of 1800 mm/s, the proportion of HAGBs is determined to be ~62%, which is larger than the value of ~57% obtained with the applied laser power of 200 W and scanning speed of 2000 mm/s. The KAM maps in Figure 7a-3,b-3,c-3,d-3 quantify the average misorientation in the range of 0.2° to 1.8° within the grains. The local grain misorientation can be used to indicate the local formation of dislocation cells and dislocation density distribution in grains [43]. When the employed VED achieves the largest value of 92.59 J/mm^3 , the proportion of misorientations <0.6° within the grains is estimated to be relatively the highest. This proportion decreases as the crystal misorientation angle grows bigger when the smaller VED corresponding to a greater employed scanning speed is applied. Furthermore, under the identical input VED of 55.56 J/mm³, the misorientation angle decreases when the laser power and scanning speed are lowered. These results suggest that the higher cooling rate in LPBF process is responsible for the greater misorientation value in KAM map because it produces (i) higher dislocation density due to the strain localization, (ii) CET of grain structures [42], and (iii) finer grain size, which has been observed to possess a higher misorientation value [44].

The preferred crystallographic growth orientation is represented by the EBSD pole figure (PF) images in Figure 8. The grains grow preferentially along {100} plane lies on xz-plane and parallel to building direction when the input VED is at the highest value of 92.59 J/mm³ (laser power of 200 W and scanning speed of 1200 mm/s). This preference weakens evidently along with the VED reducing to the lowest value of 55.56 J/mm³ (laser power of 200 W and scanning speed of 2000 mm/s), corresponding to the increasing of scanning speed. Under the same VED of 55.56 J/mm³, differences are found after the alteration of laser power and scanning speed, which indicates that texture formation does not depend entirely on the VED. The texture identified by EBSD is somewhat different from that of the XRD analysis, which is likely due to EBSD measurement being carried out on a highly localized region, where the preferred orientation alters slightly.

The microstructure of AlCoCr_{0.75}Cu_{0.5}FeNi alloy specimen produced under the VED of 92.59 J/mm³ (laser power of 200 W and scanning speed of 1200 mm/s) is presented in Figure 9. In the back-scattered electrons (BSE) image on the mechanically polished xz-plane shown in Figure 9a-1, the high magnification of grains and melt pool boundaries is revealed. The corresponding quantitative elemental distributions of Figure 9a-1 are illustrated in Figure 9a-2. The specimen in general has a homogeneous elemental distribution in the microscale, and no segregation is detected, even if the scanning speed was the slowest of 1200 mm/s. Typical cellular structures, as well as the boundaries of grains and melt pools on the electrochemically etched xy-plane, are shown in Figure 9b-1. It is noticed

distribution in grains [43]. When the employed VED achieves the largest value of 92.59 J/mm³, the proportion of misorientations < 0.6° within the grains is estimated to be relatively the highest. This proportion decreases as the crystal misorientation angle grows bigger when the smaller VED corresponding to a greater employed scanning speed is applied. Furthermore, under the identical input VED of 55.56 J/mm³, the misorientation angle decreases when the laser power and scanning speed are lowered. These results suggest in quantitative element distribution mapping displayed in Figure 9b-2 that the elements that the elements of the higher cooling of the series of t



Figriga 7e FBSB pradatises of the szeptane of AlCoCr $_{7,5}$ Cu speciments with the property of the szeptane of AlCoCr $_{7,5}$ Cu speciments with the property of the speciment of the test property of the speciment of the test property of the speciment produced by the speciment of the test property of the speciment of the test property of the speciment produced by the speciment of the test produced by the speciment of the speciment of the test produced by the speciment of the speciment of the test produced by the speciment of test produced by test produced by the speciment of test produced by test produce

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Materials 2022, 15 Figure & EBREARE images of AlGOGr0.75 Cur 5 FeNisspecimens produced by different process parameeters on (a) xy- and (b) xz-plane.



Figure 9. SEM ob **Eiseward on SEMANCE Cratice up ALNA Spectrum Fold meed with the dynamic of the second state of the second s**

The variation of cell structure morphology on the xy- and xz-plane formed under the same laser power of 200 W with the alteration of scanning speed is shown in Figure 10 Similar to the observation on grains, the cells on the xy-plane incline to being equiax (see in Figure 10a-1,b-1,c-1), while those on the xz-plane are tended to be elongated (sin Figure 10a-2,b-2,c-2). On the xy-plane, the cell size formed under the lowest scanning speed of 1200 mm/s is estimated to be ~ 0.31 um, and as the scanning speed is changed in the scanning speed is changed.

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The variation of cell structure morphology on the xy- and xz-plane formed under the same laser power of 200 W with the alteration of scanning speed is shown in Figure 10. Similar to the observation on grains, the cells on the xy-plane incline to being equiaxial (see in Figure 10a-1,b-1,c-1), while those on the xz-plane are tended to be elongated (see in Figure 10a-2,b-2,c-2). On the xy-plane, the cell size formed under the lowest scanning speed of 1200 mm/s is estimated to be ~0.31 μ m, and as the scanning speed is changed from 1500 to 2000 mm/s, the cell size is changing from ~0.28 to ~0.22 μ m, respectively. This observation concurs with our previous results [45] that the cell size decreases with the growing scanning speed. The cell structures introduced by LPBF process have been found to be beneficial for enhancing the mechanical properties owing to the high degree of dislocation induced strain hardening [46]. The spacing between the cell boundaries on IEW

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Higure 100. Alstrateware the streage sandars placed by lased by wasef 200 Weared 2008 Waapplying scar apired specel 3) of (d (1) 2) 1 20 (d = 2) 1/20 (d = 1) 1 3/20 (d = 2) 1. 500 (d = 2) 1. 500 (d = 2) - 2000 mm/s

3.3. Microhardness 3.3. Microhardness

The microhardness on the xy- and xz-plane of AlCoCr_{0.75}Cu_{0.5}FeNi specimens is presentied microphardness anthreav trandizz planenatially of reach up Early is pre septestimofigunal 10 At the national the phase mission and masses are achored management of b planes to signification of the with an the stepland and in the of its for a second the planes of the planes of the second se specigaenis iohvidnisselvalsta isdarete chevicatly roomane batchighen one ven straplage the average mi xz-olaneu Weben the VFD singlet have difference whether the state of the second state Laser power of 200 W and increasing the scanning speed from 1200 to 2000 mm/s, the When the VED input is reduced from 92.39 to 33.36 J/ mm/, maintaining constant lase hardness varies marginally (see in Figure 11a). The largest hardness 603.6 ± 6.8 HV0.05 power of 200 W and increasing the scanning speed from 1200 to 2000 mm/s, the hardness on xy-plane and 528.6 \pm 7.5 HV0.05 on xz-plane is measured from the sample produced increasing the scanning speed from 200 to 2000 mm/s, the hardness on xy-plane and 528.6 \pm 7.5 HV0.05 on xz-plane is measured from the sample produced increasing the scanning speed from 200 to 2000 mm/s, the hardness on xy-plane and 528.6 \pm 7.5 HV0.05 on xz-plane is measured from the sample produced in the sample produced i empfoying reized mm/s scanning speed: At constant VED of 5556 1/ mm, the average y-plan RANTURESS IS to Total HV Inclease HTTP 1307211 measuress from the prometer produced a proving 1200 hom 559 53 ming spessed. 1At craster www. Barka 5.56- frame & the inverse products is found the imprime law mp567e2 and 7s2 at 152 speedors Hy from 0.60 the and plane mm, b two 2005 99.5 \pm 16. and 300.0 mn2.3. And a solution of the second second the second hand ness of interview of the second strain and the second s and RD is found on both planes as plotted in Figure 12. The microhardness improves 19.5 ± 4. When the LPBF sample is denser, namely, when it possesses less porosity. HV1. In addition, a nearly linear relation between microhardness and RD is found on bot planes, as plotted in Figure 12. The microhardness improves when the LPBF sample i denser, namely, when it possesses less porosity.



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 550.1 ± 12.0 11 0.00 of the XZ plane (see in Figure 11b) with the applied fast pot and scanning speed rising from 160 W and 1600 mm/s to 200 W and 2000 mm/s, con spondingly. For comparison, the reference PECS sample exhibits a hardness of 409.5 ± HV1. In addition, a nearly linear relation between microhardness and RD is found on b planes, as plotted in Figure 12. The microhardness improves when the LPBE sample denser, namely, when it possesses less porosity.

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Figure glite Michahantess off specimens produced an (detb(a) athe Isampolase of 200 Wet with 200 W v differeifferstatismingingspeeds and (b) same WED 351551.50 mm³.

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Figure 122. Relationship betwee the menohardness rated ve lativity (RD).

3.4. Magnetic Properties 3.4. Magnetic Properties The magnetization (M-H) curves of AlCoCr_{0.75}Cu_{0.5}FeNi specimens, original powder with the anagonatization (May) szesyan of Al Carero purfer Nieperimanon original powder (PiECS) ward filter all te palitic ted as sized so and , one desplay we in Hise are lectrad los arrendess intered (RECE) as magnetization advanced in the slighted by Ktereoislas play indirin discernal allowed in ples exnisperonagybichenonbeurgeiberthetenegigebie structuresisfallesampleso Asterfeibennagnetic dissernible effertich internet attenbeumagnetication sit averete lan samples tractioner the no dis values of saturation magnetization (M_s) at 9 T of all samples are summarized in Table 4. M_s cernible effect of internal stress on magnetization; it suggests low magnetostriction. The of powder with particle class sizes of 20–63 µm and <200 µm are lower than those of the Table 4. values of saturation magnetization (40) at 300 K. PECS samples are summarized in Table 4 LPBF specimens at temperatures of both 10 and 300 K. PECS sample exhibited surprisingly Mwoff powerler invite Barticle alasses are 20-63 sumpted as 200 sum are lower than those of the nLBBE representation of the provide the second of the providence of the providen Misinglynlovo nisegmetdzationyilesenthaechalf of thas canthing. BBE dampiles canderastive lowes Mstanlowerdd medingedtsaldples. Hosene LYBP specifical munder chietiaetien aseMpower o 2011the, angene other three energiables of the second provided of the scanting spleed rate is a corresponds to the lowered colling rate. Under the same very of 35.36 f/mith, the distinction in M_s is little among the three specimens. Identical dependence of M_s on the cooling rate is revealed at 300 K. The nearly same ratio $M_{\rm s}$ (300 K)/ $M_{\rm s}$ (10 K), as well as the similar decrease of saturation magnetization, indicate a very similar saturation magnetization behavior with temperature M_s (T) and thus similar ferromagnetic Curie temperature (T_s) for decrease of saturation magnetization, indicate a very similar saturation magnetization
behavior with temperature M_s (T) and thus similar ferromagnetic Curie temperature (T_c)
for all LPBF samples. From the decrease of the magnetization, T_c can be estimated to be
well above 400 K for LPBF samples while the PECS sample exhibited T_c of about 300 K.
Coercive force of all LPBF samples is relatively low, about 760 A/m and similar to that of
Materials 2022, 15, x FOR PEER REVIEWE starting powder (480 A/m). This indicates that internal stress has only a small effect δn



Figure 13. Maspetitation (MM) over est (1)(1) to red (1) (3) 350 fr reisingling powder builbahr Geberio 25 Etc. 5 is reispensioned and reference PEC Secondlinple.

Table 4. The saturation magnetization at 9 T of raw powder, LPBF-built AlCoCr0./5Cu0.5FeNi spe	-2£
Table 4. The saturation fragmetization at 9 T of taw powder, LPBF-built AlCoCr0.75Cu0.5Fe	Ni
imens, and reference PECS sample tested at 10 and 300 K.	
specimens, and reference PECS sample tested at 10 and 300 K.	

<u> </u>					
Sample — Sample	$-10 \text{ K}^{-10 \text{ K}}$	Am (kg) 300 K	<i>M</i> s (300 K)/ <i>M</i> s (10 K) — <i>M</i> s (300 K)/ <i>M</i> s (10 K)		
Powder (20–63 μm)	71. 3^{0 К}	_{55.} 300 K	0.78		
PoRetredge(20063.mm)	$68.\overline{4}^{1.3}$	53.855.3	0.7978		
VET9 200 45 700 µm)	68.4	53.8	0.79		
(P = 200 W, v = 1200 mm/s)	80.5 _{80.5}	65.3 _{65.3}	$0.81_{0.81}$		
VEP $= 24\pi Q70 f/pm^{3}$ (P $= 290007W = 45000mm/s$)	80.180.1	64.464.4	0.8080		
VETED 555565 Jumn ³ (P = 200, W, v = 2000 mm/s)	78.7 ^{8.7}	63.0 ^{63.0}	0.80 ⁸⁰		
$VED = 55.56 J/mm^{3}$ (P = 180 %, v = 1800 mm/s) (P = 190 M v = 1800 mm/s)	78.9 78.9	63.0 63.0	$\begin{array}{c} 0.80\\ 0.80\end{array}$		
$(\Gamma - 10\psi_{\rm EM}y_{,\pm}y_{,5},50\psi_{\rm y})_{\rm H1}(\Gamma S)$	78.9	62.6	0.79		
$(P = 160 \text{ W}_{\text{F}}^{\text{ES}} \text{ should mm/s})$	78.9 _{33.9}	62.6 _{17.6}	0.78.52		
PECS sample	33.9	17.6	0.52		

Figure 14 shows the thermomagnetization (*M-T*) curves of LPBF specimens, raw powEiguand 4 estaconcet RECRE an optagratization in Ma-Routiveles of fOLMBF aspectimeness at an provaler to AdOrkfe Forther PEGE complete internship in the four of the spectra and optic spectrum and the spectrum of the spect



Higure 147 Tepperatude playlandent or genetizations circles in the simple of Algo & OB to 400 Kndr origina provider a subbitil Algo Con Concerned Strenke Speciments and reference PEGS BEGS cample.

In order to determine ferromagnetic Curie point T one of the LPBF samples fabricated in order to determine terromagnetic Curie point T one of the LPBF samples fabri K and held there tor 10 mixing the evolution of the Bolo Weitz and saturation magnetization the the paragrature of 800 I and bold there for 1A min. The evalution of the low field and saturation magnetization is approxngateropy 10 knows is the heaven in Figure d sat Alter first heating a theat Mg at 2 T and BlefikidiocceasEchapproviendatelynbrizatioAutrikktereatingmagnetizatiobedistimated tange in th the construction that the second state of the second the second state of the second en unexpected increases and then deareage of magnetization of the weak by another of the source of the second Forease at 800. Kg Differential scanning calorimetry (DSC) curve of spray-cast equiatomic tration of the spray-cast equiatomic tration of the spray cast of usition in this region [29], thus, the observed 800 K. Differential scanning calorimetry (DSC curve of spray-cast equiatomic AICoCrCuFeNi alloy indicates no phase transition in thi 1883Wah29Jcthuisgtheeleservero magastizationabehaviarindigateansomerimasmekic transi tion(s)which is tike heating can der der e Furthern Forger an other sample produced by the VEI 157.550361/grafter (lastingpotenting f 180 Wremainscanninguppeted gold 80 themer/s) dsrbiented in th ofdidating to applicated the soon reformed in their the first producting housing beautopic and Figur the device as a notice of the property of the contract of the second second second second second second second unchanged in marked with dated links in Figure 100 K. has indicates the formation of rises t three different phases. Previously, the decrease of M_s is noticed. During the cooling proces in spray-cast equiatomic AlCoCrCuFeNi alloy was found to occur at 913 K [29]. Therefore, in shift that the disappearance of A2 and B2 phase, as well as the formation of a new phich indicates the formation of three different phases. Previously, the degeneration of phich indicates the formation of three different phases. Previously, the degeneration of the different phases are constructed by the decrease of the different phases. Previously, the degeneration of the different phase is a phase of the different phase of the spinodal decomposition structures in spray-cast equiatomic AlCoCrCuFeNi alloy wa found to occur at 913 K [29]. Therefore, it is likely that the disappearance of A2 and B phase, as well as the formation of a new phase, is initiated after heating up to 1000 K.



Figure 151 Magnetic behaviors of as built Alcocents Cup Fe Nispecimens. (a) M-F curves in the range of the source of the source investigent and the the source of the source

4. Discussion

 4.1. Effect of Process Parameters on General Microstructure
 4.1. Effect of Process Parameters on General Microstructure
 The two sets of applied process parameters suggest that laser power, scanning speed, and he two frete interpalied on a cers parameters suggest that laces poweres canning speed, andaVaEletaffactritheispesimen mieturitucture der ditterentrisayo anabropanieruishthe key pairafibuetereismberinging spffijeiertiesm Sking iog speeder cantel by dowents AD the doRD at and dfurther inmicroservaturenanceatesthopeizeies. Skulanaty spreared adaptmented distribution (SIFRATEDIFOF microssita the factor that determines the nonbined influences of both last any found as we inserved and a covering the nonspeed. For instance, both laser power and scanning speed affect the local cooling rate sents the factor that determines the combined influences of both laser power and scanning during the process. It is noticed that VED alone is not sufficient to explain the differences speed. For instance, both laser power and scanning speed affect the local cooling rate dur-found in the current observations, such as RD, phase structure, grain and cell size, crystal ing the process. It is noticed that VED alone is not sufficient to explain the differences misorientation, texture, and microhardness. It is in accordance with previous research 147/ tound in the cupper to have over the constant of the constant of the cupper to the cup miserientationratexture condiministration of the condiministration of the province of the prov [47]) threehigt a theterp phical biliey con MED optimized it the laPB by loaved. Has the en over eathed, as it failes toroktersibeed to be taken intercomplice phipsics in the to PBF uped etser The restandings proposed final anoraties parameters normalized anthanky bankers around the provent of the provide the provided of thermine the optimal process parameters in which the influences of process parameters in the optimal process parameters in which the influences of process parameters and physical properties such as thermal conductivity have been considered [48,49]. understanding and final properties. For instance, normalized enthalpy has been proven I hree types of defects are identified in the as-built specimens, i.e., fack-of-fusion, to be effective to determine the optimal process parameters, in which the influences of spherical gas pores, and cracks. The fack-of-fusion defect occurs when the employed procession personal procession of the properties of the properties of the procession of the procesion of the procession of the procession of the procession sidarach48A9bct is shown earlier in Figure 3c. In addition, it is found that when the laser poWhreeathposheflangesttspartiedtealtified 200 Wethe-lauklospesimetrseite.anathrouedusion,

spherinalizated of the service of th rameterinsonsplateinaltinadiffectienpnearnebanithedeverepowernie tedeverdeetse Asteliample of suggest that both laser power and VED are required to be at a sufficiently high level to avoid the lack-of-fusion defects. The spherical gas pores, according to former research [50] power reaches the largest applied value of 200 W, the lack-of-fusion defects are formed can be induced by (a) the gas pores pre-existed in the gas atomized powder. (b) entrapment when the VED input is the lowest (5) for the evaporation of volatile element. The most morgaine on plete in all in gesteries and a period of the second of the suggest that both inequores were and VED har to seguined to the at the up is supported by level to avolisterhedla Elkentforesitoris defected That spherical egast from the protecting tan hospitererose arch [50] then goe an university of a) RRE Elesspores processific the due for the further investigation der, (b) entrapment of the protective Ar atmosphere, or (c) the evaporation of volatile element. The most volatile element in the present work is aluminum, however, no aluminum was found in association with the pores even though the loss of aluminum in the LPBF samples was observed. Therefore, it is expected that the pores result from the protective atmosphere of either gas atomization or LPBF. This needs to be confirmed by further investigation.

The highest density is achieved in the sample produced with the maximum VED of

The highest density is achieved in the sample produced with the maximum VED of 92.59 J/mm³. Most of the porosity in this sample is due to cracks, unlike those obvious lackof-fusion defects and gas pores observed in other samples built with lower VED. The high crack sensitivity during the LPBF process has been reported in the LPBF-built equimolar AlCoCrCuFeNi HEA [20]. It is known that generally in LPBF process, internal stresses and localized strains would be created due to thermal gradient during the process [51]. In addition, the misorientation of boundaries contributes to the cracks propagating along the HAGBs instead of the LAGBs, as revealed in Figures 3 and 7. This corroborates previous research, where it was described that HAGBs exhibit a higher cracking sensitivity than those of LAGBs [52–54]. In this research, these intergranular cracks are likely to be solidification cracks [55].

As discussed above, cracking is related to the proportion of HAGBs, and the cracks would affect the RD. The microhardness of the LPBF samples appears roughly to be a function of RD, as depicted in Figure 12, while grain size and cell size have smaller effects within the range studied. As the RD reduces, the measurement error of each hardness value varies more significantly. The highest hardness of 604.6 ± 6.8 HV0.05 on the xy-plane is achieved with the highest RD of ~97% when the HAGBs have the lowest value of ~45%. However, it is observed that the RD of each specimen produced under the laser power of 200 W with a different scanning speed of 1500 and 2000 mm/s is similar (see in Figure 2a), while the hardness of specimen produced with a scanning speed of 2000 mm/s is higher. Moreover, the RD of specimens produced under the constant VED of 55.56 J/mm³ with the laser power and scanning speed of 160 W and 1600 mm/s and 180 W and 1800 mm/s is noticeably lower than that of 200 W and 2000 mm/s (see in Figure 2b), but the distinction on the hardness is not as obvious (see in Figure 11b). This suggests that although the RD is relatively lower, the hardness is enhanced by the smaller cell size induced by increasing the scanning speed, as displayed in Figure 10. This is likely to be ascribed to the higher density of dislocations associated with the cells [56]. In conjunction with the controllability of the structures, especially cell size, implies the great potential of designing alloys with the desirable properties.

4.2. Effect of Microstructure Evolution on Magnetic Properties

The representative values of M_s of as-built LPBF specimens and raw powder are summarized in Table 5. These values were higher than those reported previously for similar compositions also highlighted in the same table. For comparison, Zhang et al. [28] obtained the M_s of 38.2 Am²/kg (at 1.5 T and room temperature) on as-cast AlCoCrCuFeNi alloy. The M_s of as-cast and splat-quenched AlCoCrCuFeNi alloy was disclosed by Singh et al. [32] to be 44.0 and 46.0 Am²/kg (at 14 T and 300 K), respectively.

Table 5. The saturation magnetization of multicomponent alloys produced by various methods.

Alloy	Method	$M_{\rm s}$ (Am ² /kg)	Annealing Temperature and Time	$M_{ m s}$ after Annealing (Am ² /kg)	Ref.
AlCoCr _{0.75} Cu _{0.5} FeNi (powder, 20–63 μm)	Gas atomization	55.3 (at 9 T and 300 K)	-	-	This work
AICoCr _{0.75} Cu _{0.5} FeNi (VED = 92.59 J/mm ³ ($P = 200 \text{ W}, v = 1200 \text{ mm/s}$))	LPBF	65.3 (at 9 T and 300 K)	-	-	This work
AlCoCr _{0.75} Cu _{0.5} FeNi (VED = 55.56 J/mm ³ ($P = 180 \text{ W}, v = 1800 \text{ mm/s}$))	LPBF	60.1 (at 2 T and 305 K)	800 K, 10 min	75.9 (at 2 T and 305 K)	This work
AlCoCrCuFeNi	Splat quenching	46.0 (at 14 T and 300 K)	-	-	[32]
AlCoCrCuFeNi	Casting	44.0 (at 14 T and 300 K)	-	-	[32]
AlCoCrCuFeNi	Casting	38.2 (at 1.5 T and room temperature)	1273.15 K, 2 h	16.1 (at 1.5 T and room temperature)	[28]
$Fe_{15}Co_{15}Ni_{20}Mn_{20}Cu_{30}$	Homogenization	12.0 (at 2 T and 300 K)	873.15 K, 240 h	21.0 (at 2 T and 300 K)	[33]

The spinodal decomposition in AlCoCrCuFeNi alloy has been well established [13,29,30,32]. It has been shown that the phase decomposition already occurs at the early stage of

solidification of the melt even under a high cooling rate of 10^6 – 10^7 K/s [32]. Particularly, the phase decomposition into BCC A2 and B2 structures has been observed in the gasatomized raw powder, as shown in Figure 4. During the LPBF process, as the scanning speed varies from 2000 to 1200 mm/s under the same laser power of 200 W, accordingly, $M_{\rm s}$ increases from 78.7 to 80.5 Am²/kg at 10 K, and from 63.0 to 65.3 Am²/kg at 300 K. The differences identified in the saturation magnetization M_s of specimens (depicted in Figure 13 and summarized in Table 4) can thus be related to the dependence of $M_{\rm s}$ on the degree of spinodal decomposition, which is controlled by the cooling rate. The high cooling rate in the LPBF process leads to the suppressed decomposition, i.e., less Fe-Cr-rich A2 phase while more Al-Ni-rich B2 phase structure is produced, which causes the decrease of $M_{\rm s}$. This is in agreement with previous research [25,31], in which the Al-Ni-rich ordered BCC phase possessed weakened ferromagnetism. Singh et al. [32] showed that in the as-cast AlCoCrCuFeNi alloy aged at 873.15 K for 2 h then followed by an ice quenching, the $M_{\rm s}$ increased by 4 Am²/kg at 14 T and 300 K. This improvement is comparable to our results by varying the input parameters in LPBF process, as listed in Table 4. It demonstrates that LPBF provides an efficient method to enhance the magnetic properties without the need for time-consuming heat-treatment. Furthermore, it allows a local control of magnetic properties via input parameters of the LPBF process.

The variations of M_s after annealing has also been given in Table 5. Interestingly, the M_s of one LPBF specimen in this research is found to increase by approximately 15 Am²/kg at 2 T and 305 K after annealing at 800 K for 10 min, as displayed in Table 5. The enhanced M_s indicates that the annealing temperature around 800 K falls into the miscibility gap of spinodal decomposition, which promotes the further formation of ferromagnetic A2 structure. It suggests that if annealing this alloy at the temperature of 800 K for a suitable period, it is possible to improve the M_s significantly. As a comparison, in the research conducted by Rao et al. [33] displayed in Table 5, the Fe₁₅Co₁₅Ni₂₀Mn₂₀Cu₃₀ HEA specimen was annealed at 873.15 K for 240 h to achieve an improvement from 12 to 21 Am²/kg at 2 T and 300 K.

When further heating up to 1000 K, the temperature is out of the range of miscibility gap, and the phase transition is also initiated. Zhang et al. [29] stated that the annealing of the spray-cast sample results in the disappearance of spinodal decomposition structures and the formation of new phases. The latter is also observed in our case (Figure 15b). Consequently, the $M_{\rm s}$ of LPBF specimen decreased while heating up to 1000 K. Moreover, it also explains the smallest $M_{\rm s}$ detected in the PECS sample. The PECS sample is sintered at the temperature of 1273.15 K, which is above the miscibility gap of spinodal decomposition, similar to the as-cast sample annealed at 1273.15 K for 2 h exhibiting the $M_{\rm s}$ of 16.1 Am²/kg (at 1.5 T and room temperature) [28], as displayed in Table 5. The cooling rate of 100 °C/min in the reference PECS sample is much lower than that in the LPBF process. The slow cooling process leads to the formation of dual-phase FCC + BCC structures (see in Figures S1 and S2), which is in accordance with the former investigations on AlCoCrCuFeNi based alloy produced by traditional methods with a slow cooling rate [7,9]. The BCC phase in the PECS sample is determined to be Al-Ni-rich (see in Figure S3 and Table S2). As the Al-Ni rich BCC phase discloses a weakened ferromagnetism [25,31], and furthermore, ferromagnetism is known to be sensitive to the aging temperature [57], the annealing and slow cooling are likely responsible for the smallest $M_{\rm s}$ of PECS sample (Table 4).

It can be therefore summarized that there are two stages of phase decomposition in the AlCoCrCuFeNi based alloy. When the melt solidifies at a high cooling rate, generally $\geq 10^3$ K/s, the phase separation into Fe-Cr-rich A2 and Al-Ni-rich B2 phase occurs. As the increase of cooling rate suppresses the formation of A2 phase, it results in the lower saturation magnetization. Once the sample is annealed at the temperature located in the miscibility gap of spinodal decomposition, further decomposition occurs, leading to the enhanced magnetization M_s . At a low cooling rate, such as in a regular casting process, dendrites and interdendrites are formed, including the Cr-Fe-Co-rich regions, and if annealing the sample at a temperature fell into the miscibility gap, the Cr-Fe-Co-rich regions are separated into the ferromagnetic Fe-Co-rich structure and antiferromagnetic Cr-rich structure, and a higher degree of decomposition results in the larger M_s , as disclosed by Singh et al. [32].

In this case, the magnetization measurements proved to be an efficient method to distinguish the various structural phases down to the nanoscale, which might be tedious to achieve by other characterization methods. Based on the relationship among cooling rate, degree of spinodal decomposition, and magnetization, with the great controllability of LPBF, it is feasible to design the magnetic properties as demanded.

5. Conclusions

To conclude, the microstructure and properties of additively manufacturing $AlCoCr_{0.75}Cu_{0.5}FeNi$ alloy with LPBF process have been investigated. The feasibility of utilizing spinodal decomposition to induce the improvements of magnetic properties in multicomponent alloys is presented, and this can be easily materialized by the LPBF process.

- Two sets of process parameters have been employed, namely, the different VEDs corresponding to the alteration of scanning speed under the same laser power, and the same VED referring to different laser power and scanning speed. The observations demonstrate that these three parameters contribute to the different aspects during the process, and they should all be optimized to achieve the best results.
- 2. All LPBF specimens are found to consist of BCC phase, while the reference PECS sample contains both FCC and BCC phase. The phase structure in LPBF specimens estimated by XRD reveals that the A2 structure formation is suppressed by the increasing cooling rate. Smaller cellular structures are formed by employing a higher scanning speed under the same laser power. This contributes to the high microhardness of 604.6 ± 6.8 HV0.05, despite the cracks and other defects. It is noticeably higher than 409.5 ± 4.2 HV1 of the reference PECS sample.
- 3. Raw powder, LPBF specimens, and PECS sample all exhibit soft magnetic behavior. The highest M_s of 65.3 Am²/kg is reached in as-built alloy. The saturation magnetization is related to the spinodal decomposition into A2 and B2 phase structure, and the degree of decomposition is controlled by the cooling rate, which can be adjusted by means of altering the scanning speed in the LPBF process. As the scanning speed declines, corresponding to a decreased cooling rate, a higher degree of decomposition is conducted, leading to the formation of a larger fraction of A2 structure. It contributes to the enhancement of M_s comparable to the formerly reported value of the as-annealed sample, yet without the need for time-consuming post treatment. In addition, the decomposition is furthered via annealing at 800 K for 10 min, resulting in the increase of M_{s} , approximately by more than 15%.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/ma15051801/s1, Figure S1: XRD experimental and refinement patterns of PECS AlCoCr_{0.75}Cu_{0.5}FeNi alloy; Figure S2: Secondary electron (SE) image of PECS AlCoCr_{0.75}Cu_{0.5}FeNi alloy; Figure S3: SEM-EDS results of PECS AlCoCr_{0.75}Cu_{0.5}FeNi alloy. (a) Secondary electron (SE) image. EDS spectra of (b) Point 1 and (c) Point 2 indicated in (a); Table S1: Archimedes density and Vickers hardness of PECS AlCoCr_{0.75}Cu_{0.5}FeNi alloy; Table S2: Chemical compositions of Point 1 (FCC phase) and Point 2 (BCC phase) displayed in Figure S3.

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