Additive manufacturing of an Fe–Cr–Co permanent magnet alloy with a novel approach of in-situ alloying

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ABSTRACT

Additive manufacturing has become increasingly important in the production of magnetic materials in recent years due to the great demands for miniaturization and complex-shaped magnet parts. In this study, the laser beam-powder bed fusion process (LPBF) has been used to develop an in-situ alloying process for the additive manufacturing of a permanent magnet material of the Fe–Cr–Co system. This novel method allows for the production of complex alloys with a chemical composition suited to each specific case of application, achieved by using elemental powders or simpler commercial alloy powders as base materials. The core focus of this study has been on the development and characterization of the printing process using a Fe-30.5Cr-15Co-1.5Mo alloy. The in-situ alloying process has been developed by performing melt pool tests on the two main component powders Fe and Cr and by conducting parameter studies using two different powder mixtures with different sphericity of their components. The influence of different printing parameters and post-printing treatments on the chemical homogeneity and magnetic properties has been studied for selected samples. In addition, magnetic measurements at different temperatures have been performed to investigate the temperature stability of the magnetic properties of the 3D printed material.
IMPACT STATEMENT
As by today, the current amount of research done on the additive manufacturing of magnetic materials is rather low. Most of research is focused on rare-earth containing magnetic materials. In this work therefore, we are taking another direction in which we will show that LPBF combined with in-situ alloying is an ideal method for the production of a great variety of different rare-earth free magnetic materials. The positive results of our work can both have an influence on the scientific community, as further research in the field on different promising rare-earth free magnetic materials is to be expected. Furthermore, a positive economic impact may occur since the production of rare-earth free magnetic materials is dependent on different raw material sources which are both more cost-effective and less critical in terms of their supply chain. This effect is also accompanied by a positive environmental impact, since the mining of rare-earth metals usually comes with considerable environmental pollution.

1. Introduction and incentives
Additive manufacturing of magnetic materials has been a research topic of increased interest in recent years (Chaudhary, Mantri, Ramanujan, & Banerjee, 2020; Huber et al., 2017; von Petersdorff-Campen et al., 2018; Compton et al., 2018; Khazdozian et al., 2019; Huber et al., 2016; Li et al., 2018; Li, Post, Kunc, Elliott, & Paranthaman, 2017; Li, Tirado, et al., 2017; Kishore et al., 2017; Li et al., 2016; Volegov et al., 2020; Skalon et al., 2019; Urban, Meyer, Kreitlein, Leicht, & Franke, 2017; Huber et al., 2019; Bittner, Thielisch, & Drossel, 2020; Bittner, Thielisch, & Drossel, 2021; Paranthaman et al., 2016). One of the most common hard-magnetic materials in this field of research at the present time is Nd–Fe–B, which is one of the strongest hard-magnetic materials currently available on the market due to its superior magnetic properties (Woodcock et al., 2012).

This material, Nd–Fe–B, however also comes with a number of disadvantages in terms of both its intrinsic properties and its applicability in additive manufacturing which can be listed as following:

- its magnetic properties are not stable at higher temperatures (Li et al., 2020).
- it is a critical material in terms of availability and sustainability due to its high rare-earth metal content (Haque, Hughes, Lim, & Vernon, 2014; Simoni, Kuhn, Morf, Kuendig, & Adam, 2015; EU Policy, European Raw Material Alliance).
it has difficult processability in powder-based melting techniques leading to low densities of additively manufactured parts (Skalon et al., 2019; Urban et al., 2017; Bittner et al., 2020; Bittner et al., 2021).

Nd–Fe–B is listed by the European Union as a critical raw material due its importance in devices for sustainable energy production (EU Policy, European Raw Material Alliance) and in fields, where miniaturization and an increase in complexity of the strongest magnetic parts are required; it cannot be replaced by other currently available materials.

However, due to mentioned above disadvantages of Nd–Fe–B, another field of research has been revitalized in recent years, focusing on the improvement of rare-earth-free magnetic materials. At the forefront of this are Fe–Co-based materials, such as Al–Ni–Co and Fe–Cr–Co. The magnetic properties in these materials depend on a spinodal decomposition of a bcc $\alpha$-phase into a bcc, magnetic $\alpha_1$-phase, and a non-magnetic $\alpha_2$-phase. The $\alpha$-phase decomposition occurs at a specific temperature of immiscibility which is characteristic of each alloy and composition. At this temperature, a thermomagnetic heat treatment is applied for an optimal phase structure to obtain hard-magnetic properties, followed by subsequent step-wise cooling to a lower temperature. In this instance, magnetic needle-shaped $\alpha_1$-phases are formed, embedded in a non-magnetic or weak magnetic $\alpha$-matrix providing the good hard-magnetic properties (Zhou et al., 2019; Mukhamedov, Ponomareva, & Abrikosov, 2017; Minowa, Okada, & Homma, 1980).

Additive manufacturing of Al–Ni–Co has been successfully carried out in two subsequent studies with LENS/DED and EBM/PBF by White et al. (2017) and White et al. (2019). Although being a brittle material, successful implementation of different printing processes has been performed and the potential for this material in additive manufacturing has been demonstrated.

The research on Fe–Cr–Co has been primarily focused on possible methods to improve the magnetic properties in this material either by the addition of alloying elements (Mohseni Zonoozi & Kianvash, 2020; Tao, Ahmad, Khan, Zhang, & Zheng, 2019; Tao, Ahmad, Zhang, Zheng, & Zhang, 2020; Tao, Ahmad, Zhang, et al., 2019; Gao, Gong, Wang, Qu, & Huang, 2015; Wu et al., 2017) or the introduction of plastic deformation (Korznikova, 2006; Korznikova, Korneva, Korznikova, Institute for Metals Superplasticity Problems, & Russian Academy of Science, 2020) to improve the microstructure. Research on the use of additive manufacturing in the production of this material has not yet been published to our best knowledge.
Both materials present a promising alternative for Nd–Fe–B magnets in fields where miniaturization and a high shape-accuracy are required and where properties as strong as those for the rare-earth-containing counterparts are not required or in areas, where a low loss of the magnetic properties with increasing temperature and high operating temperatures are needed (e.g., some electric engines). This work therefore constitutes a first approach to the additive manufacturing of an Fe-30.5Cr-15Co-1.5Mo alloy, located farther on the Cr-rich side of the ridge region in the Fe/Co–Cr quasi-binary phase diagram, with in-situ alloying which is a promising method for future alloy development in additive manufacturing (Mosallanejad, Niroumand, Aversa, & Saboori, 2021).

2. Methodology

2.1. Equipment

Laser powder bed fusion (LPBF): ORLAS Creator from Coherent with a max. 250W, Yb:YAG laser source with a wavelength of 1067nm and a beam diameter of 40–120 nm. Process Gas: Air Liquide ALPHAGAZ™; purity 5N; humidity < 3.0 ppm/mol, oxygen content < 2.0 ppm/mol, and hydrocarbons < 0.5 ppm/mol.

Scanning electron microscopy (SEM) investigations: Tescan REM-Mira3 Scanning electron microscope, 30 kV max. acceleration voltage.

Energy dispersive X-ray (EDX) investigation: AMETEK EDAX Octane Super-A EDX detector (sensor area: 60 mm²).

X-Ray crystallography (XRD) investigations: Rigaku MiniFlex Benchtop X-ray diffractometer.

Light optical microscopy: Zeiss Axio Vert.A1 MAT light optical microscope for materials analysis, Zeiss ZEN core for image capture and analysis magnetic measurements: Magnetic measurements are realized using an in-house extraction magnetometer installed in a 7T superconducting coil at Neel Institute. M(H) curves are recorded at various temperatures ranging from room temperature up to 800 K.

Powder flowability: Hall Flowmeter according to EN ISO 4490.

Measurement of particle size distribution (PSD): Malvern Instruments Mastersizer 2000 Particle Size Analyzer with Hydro 2000SM (AWM2002) Dispersion unit.

Metallography: Struers Tegramin-30 automatic, microprocessor-controlled machine for grinding and polishing of specimens (300 mm MD-Disk); QATM saphir vibro vibropolishing machine.
Hardness measurement: **EMCO-TEST M1C010** automatic hardness measurement device.

Software for evaluation: **MATLAB, ORLAS Suite, Origin.**

### 2.2. Process development: melt pool tests

Melt pool tests were carried out to determine an area of printability, in accordance with Skalon et al. (2019). On the two main component powders Fe and Cr. Single layers with a layer height of 25 um were printed on stainless steel platelets (see Figure 1(a)) out of both Fe and Cr powders in the following range: laser power 25–250 W and scan speed 100–1500 mm/s. The platelets with the single melt tracks were cut in half
and one cross-section each, subsequently polished with a SiC foil (size 4000) and the top-down view images were collected via SEM imaging (see Figure 1(a–c)). The melt tracks were sorted into three categories (as can be seen in Figure 1(b,c)):

1. occurrence of balling (Rayleigh, 1892; Rombouts, Kruth, Froyen, & Mercelis, 2006; Perihan, 2018);
2. no balling observable with a wetting angle below 90°;
3. no balling observable with a wetting angle above 90°.

The occurrence of balling was determined qualitatively, visually and the wetting angle was determined using the SEM software and the average of these two values was considered for the further analysis. The stability condition was set at a wetting angle above 90° according to Skalon et al. (2019) and Gusarov and Smurov (2010). Based on these results, an area of printability for further studies as determined by the parameters fulfilling category 3 as shown in Figure 7 was determined.

2.3. Process development: influence of powder quality

The influence of powder quality on the printing process was investigated using two powder mixtures (A and B) consisting of elemental powders of different qualities to print samples using a defined parameter matrix based on the melt pool tests.

Two kg of each powder mixture were mixed for 3 h with 50 rpm speed in a rotational mixer with three stainless steel balls with a diameter of 12 mm to ensure proper mixing and to avoid coagulation of the powder particles. The powders were mixed to achieve the desired composition after in-situ alloying, SEM images of the powders as well as results of the measurement of PSD can be seen in Figure 2, the manufacturers and specifications of the elemental powders used in the caption. In the case of both powder mixtures, the two main components Fe and Cr were added by using the same elemental powders. Both of these powders were of good quality with the sphericity and the PSD in the suitable range for the LPBF process.

Additionally, for powder mixture A, a Co–Cr–Mo alloy was used for adding the remaining elements, Co and Mo, to the composition and the share of pure Cr powder therefore needed to be decreased. The Co–Cr–Mo alloy also had optimal properties for the LPBF process, which are a high degree of sphericity and a PSD in the suitable range of 10–63 µm. For powder mixture B, pure Co and Mo powders were added. However, the PSD was much finer than the PSD of the
powders used for mixture A and the morphology was less suitable for the process. A lower quality of the printed parts therefore was anticipated.

After mixing, flowability tests were performed and the thoroughly mixed powders were then used in the printing of the test samples. When measuring the flowability of both powder mixtures, the flowability of neither was sufficient to allow a flow through the hole in the cylinder of the Hall flowmeter. It was thus only possible to conduct a visual, qualitative analysis of the spreadability in the printing chamber. Nevertheless, powder mixture A exhibited a notably better coverage of the printing bed than powder mixture B, as can be seen in Figure 3. In particular, the spreadability of the powder in the printing chamber seemed to increase upon flooding the chamber with argon protection gas. This could be attributed to chemical and magnetic interactions of the paramagnetic oxygen present in regular atmosphere attached to the powder particle surface with the ferromagnetic iron particles which could hinder the flowability and spreadability under these conditions (Chen et al., 2020).

Thirty-six samples were printed from each powder in the first batch to determine the influence of energy density and laser power on the quality of the printed parts. Other parameters like spot size (BED), hatching distance (HD), and layer height (LH) were kept constant at 50, 60, and 25 μm, respectively. The parameters applied can be found in Table 1, the oxygen content of the atmosphere was kept below 0.1%.

Figure 2. a) SEM images of the powder mixtures used for the parameter studies. b) Results of measurement of particle size distribution. Spherical Fe and Cr powders were purchased from ECKART TLS Technik GmbH with a PSD of < 63 μm and < 53 μm, respectively. Spherical CoCrMo powder (MetCo 78 A) was purchased from Oerlikon GmbH with a PSD of 15–53 μm. Non-spherical Co and Mo powders were purchased from US Research Nanomaterials Inc. with a PSD of < 10 μm and < 800 nm, respectively.
2.4. Material characterization: homogeneity and density

For homogeneity and density analysis, samples printed from both powder mixture were cut in xy- and xz-direction (definition of axes in Figure 4) for metallographic preparation by grinding (SiC foil 800–4000, 3 min each), polishing (1 um, soft cloth, 30 min) and subsequent vibropolishing (Eposal 0.06 um, LAMBDA cloth, overnight).

To get an estimation of the density of the samples, three 4.5 × 3.2 mm light optical images were taken of the cross sections of each sample and analysed both visually and with an in-house developed Matlab script.

To determine the influence of printing parameter on the elemental homogeneity in the in-situ alloyed material (samples of powder mixture A only), EDX element distribution maps of Fe, Cr, and Co were taken in an area of 800 × 650 um, using an acceleration voltage of 20 kV, a beam intensity of 16, a dwell time of 100 us and a resolution of 512 × 400. Three EDX maps and as a reference, three EDX maps of a fully annealed sample (1100 °C, 1 h, argon atmosphere) were taken from each of the 15 selected samples from the parameter matrix. The images of the EDX maps were further processed in MATLAB to obtain a numerical value for the degree of inhomogeneity by a three-step calculation:

1. the corresponding distribution map was converted into a grayscale image for each element.
2. the luminance values of the grayscale images were ordered in a histogram plot.
3. A two-term Gaussian fit was used to determine the peak positions of the histogram plot.

The average value of the three peak positions obtained for the reference was calculated and the difference between this peak position and the peak position obtained for each map was calculated. The average of the three values obtained from three maps for each sample was used as a value of inhomogeneity of Fe, Cr, and Co distribution in the sample. The MATLAB scripts used for homogeneity and density analysis can be found in the Supplementary data. A graphical interpretation of the analysis can be seen in Figure 5.

2.5. Materials characterization: determination of the miscibility gap

Measurements according to Kaneko et al. were performed to investigate the spinodal decomposition in the 3D printed and homogenized sample and to determine the temperature of immiscibility (Kaneko, Homma, Nakamura, Okada, & Thomas, 1977). Bars of 15×85×15 mm were printed (printing parameter: \( P = 190 \text{ W}, E = 2.8 \text{ J/mm}^2 \)), homogenized at 1100°C for 1 h, annealed at 510°C for 50 h and afterwards cut into samples of 15×5×15 mm parallel to the building direction. The samples were heat treated in air for 30 min at different temperatures from 520 to 700°C in steps of 10°C and subsequently quenched in water. The heat treatment was repeated under the same conditions except for the use of air cooling instead of water quenching. The hardness was determined by performing 25 hardness measurements (HV10/15) for each sample in a grid of 5×5|1.25 mm. This procedure was carried out to detect possible inhomogeneities parallel to the building direction and to get a precise value for the hardness of each condition.
2.6. Materials characterization: magnetic measurements

To determine the influence of printing parameters and post-printing treatments on the magnetic properties, four samples were printed according to the geometry shown in Figure 4. For magnetic measurements, cylinders with a diameter of 3 mm and 3 mm height were cut out of the samples parallel to the building direction. The process parameters were chosen to investigate the influence of homogenization, two different annealing treatments and of energy input during printing on the magnetic properties. Selected samples were measured parallel and perpendicular to the building direction to determine, if an anisotropy in magnetization was present in the material. The homogenization treatment was performed at 1100 °C for 1 h, the annealing treatments can be seen in Figure 6 and all process conditions and results summarized can be seen in Table 2. M(H) hysteresis measurements were performed at different temperatures for selected samples to determine the temperature stability of the magnetic properties.

3. Results and discussion

The results of the melt pool tests can be seen in Figure 7. A large number of stable parameters seem to be located at laser powers of 130 W and above with the most stable parameters located above 160 W, due to

**Figure 5.** Strategy for the analysis of inhomogeneity in the in-situ alloyed samples: The colour-coded maps were converted into grayscale images and the luminance values plotted in a histogram plot. The peak positions were determined via a Gaussian fit, of which the difference between the average value of three reference samples and the map investigated was determined as a value of inhomogeneity for each map. Three element distribution maps were recorded and processed in this manner for each sample for which subsequently an average value of inhomogeneity was calculated.
Figure 6. Annealing treatments applied to the samples for magnetic measurements. Hardness values after heat treatment: 452HV for 640HT, 470HV for 510HT. This indicates the occurrence of a spinodal decomposition in both cases, as shown by Kaneko et al. (1977).

Table 2. Process and post-process conditions applied for the selected samples and results of the magnetic measurements.

| Sample # | Laser power [W] | Energy density [J/mm²] | Homogenization | Heat treatment | $\mu_0H_C$ (kA/m) | $\mu_0M_r$ (T) | $BH_{max}$ (kJ/m³) | Anisotropy |
|----------|-----------------|------------------------|----------------|---------------|------------------|----------------|------------------|------------|
| 1        | 240             | 400                    | No             | 640HT         | 22               | 0.42           | 0.08             | No         |
| 2        | 240             | 400                    | 1100 °C–1 h    | 640HT         | 19               | 0.47           | 0.08             | No         |
| 3        | 240             | 400                    | 1100 °C–1 h    | 510HT         | 1                | 0.10           | 0.08             | No         |
| 4        | 240             | 160                    | 1100 °C–1 h    | 640HT         | 19               | 0.52           | 0.08             | Yes        |

A description of the heat treatment can be found in Figure 6.

Figure 7. Results of the melt pool study for pure Fe (a) and pure Cr (b). An area with lower energy input with good and bad parameters according to the melt pool tests was chosen for the subsequent parameter studies (marked with a black box).
the fact that at 160 W and below balling appears to occur at lower energy densities, below 3 J/mm². Additionally, the stability range for printing pure Fe appears to be larger than when printing pure Cr. A subsequent parameter study was carried out to test the validity of the melt pool study. In this study, cuboid samples have been printed with parameters located in a region with mixed good and bad results according to the melt pool study as indicated by the black box in Figure 7 and the relative density of the printed parts has been taken as an indicator of the quality of the chosen parameter. The results of the study can be seen in Figure 8.

The results of the parameter study can be seen in Figures 8 and 9. Figure 8 shows the results of the density measurements performed on those samples which it was feasible to print. As can be seen, no stable samples could be printed with a laser power of 25 W, regardless of the energy density applied. This is in good correlation with the predictions of the melt pool tests, where no stable melt tracks could be obtained with a laser power of 25 W. The melt pool studies also predicted no stable samples for laser powers between 60 and 100 W. It was possible to obtain them in the parameter study, however with higher energy inputs. For laser powers between 100 and 160 W, unstable parts were predicted at lower energy densities, which is also in good correlation with the results of the parameter study, where lower densities were obtained in parts printed with lower energy densities.

When comparing the influence of the two powders observed, the apparent densities of the parts printed with powder mixture B are significantly lower than those of the sample printed with powder mixture A. This can also be seen in the light optical micrographic images of

![Figure 8](image.png)

**Figure 8.** Results of the measurement of apparent densities of samples printed from powder mixtures A and B measured with the Archimedes method.
cross-sections of three selected samples printed with different energy densities from both powder mixtures as shown in Figure 9. In all six samples, both small pores formed by gas entrapment during solidification due to excess energy, as well as residual, unmolten Cr particles can be found, although the amount of these particles seem to decrease with increasing energy density. Lack-of-fusion defects in samples printed with powder mixture A only seem to occur in the specimen printed with low energy density (1.6 J/mm²), probably at the edge of the melt pool due to a lack of energy to melt the powder. An etching method to make the melt pools visible and to test this hypothesis however could be neither found in literature nor developed in the timeframe of this work. In samples printed with powder mixture B, lack-of-fusion defect occurred in all samples, regardless of the energy input. Moreover, the distribution
of pores appears to be more inhomogeneous in these samples, as is also indicated by the much larger standard deviation in density. This can be also seen in all cross-section images which have been put in the Supplementary data. The increased occurrence of lack-of-fusion defects can be explained by the worse spreadability of this powder mixture resulting in insufficient coverage of each layer in the powder bed during printing. At areas, where no powder is distributed, the passing laser beam remelts the previous layer which can lead to the formation of cavities in the material. In this manner, these cavities can grow in size and subsequently, lack-of-fusion defects can be formed either by insufficient filling of these cavities due to a bad flowability of the powder mixture or by the insufficient energy available to melt the powder in locally restricted areas with large layer height which can be formed when filling larger grown cavities (Zhang, Li, & Bai, 2017; Wang, Dai, Liao, & Zhu, 2020). An inhomogeneous distribution of lack-of-fusion defects in the sample may be a confirmation of this hypothesis, since local defects in the powder bed can appear randomly during power distribution. As a result of the difference in spreadability of the two powder mixtures, the quality of the parts produced from the mixtures with overall identical chemical composition is vastly different.

Upon further analysis of the influence of laser power and energy density on the apparent density of the parts, it seems as if the apparent densities improve with both increasing energy density and laser power for both powder mixtures. This effect seems to be present in samples printed of both powder mixtures and Shoji Aota, Bajaj, Zschommler, Sandim, and Aimé Jägle (2020). Also observed higher densities in in-situ alloyed steel samples printed with a similar layer height when using an energy density above 2.5 J/mm².

The results of the homogeneity analysis for each element can be found in Figure 10(a–c). The results suggest that the degree of inhomogeneity

![Figure 10](image-url)

**Figure 10.** Results of the homogeneity analysis measured in xy-direction according to Figure 3 for the applied printing parameters showing the inhomogeneity in elemental distribution of a) Cr; b) Fe; c) Co. Values measured in xz-direction are very similar to the values seen here and are therefore not explicitly shown. These values can be found in the Supplementary data.
is dependent on both the applied laser powers and the energy densities, and with a differing in magnitude for each element. The lowest inhomogeneity was obtained for Co, the highest for Cr. It can be explained by the different melting points of each of the base materials used. The CoCr powder as the only source of Co, has a melting point of 1423°C as indicated by the manufacturer (Material Data Sheet – Oerlikon Metco 78A), while the melting temperatures for Fe (1538°C) and Cr (1907°C) powders are both higher, therefore possibly resulting in a greater degree of inhomogeneity due to the higher energy input needed for melting in the LPBF process. Another possible reason for the much higher inhomogeneity in the Cr distribution of the samples could also be that the Cr is distributed from two sources, firstly from the low-melting CoCr alloy and secondly, from the high-melting pure Cr powder. A visible correlation also can be seen between the degree of inhomogeneity and the energy input applied. Consistent with previously mentioned hypothesis, a higher energy input results in a lower degree of inhomogeneity for each of the three elements for each laser power applied. The correlation between applied laser power and inhomogeneity, however, would appear to be less straightforward. The lowest inhomogeneities seem to be achieved at medium to upper laser powers (145 W and 190 W). A possible explanation for this correlation might be that specific heating and cooling rates correlated to the laser power are causing a better mixing in the melt track.

These results are also in agreement with Shoji Aota et al. (2020). The highest degrees of inhomogeneity were also found for Cr, which also decreased with increasing energy input.

The results of the hardness measurements can be seen in Figure 11(a). The hardness decreases subsequently with increasing annealing

Figure 11. a) Hardness measurements to determine the Miscibility Gap in Fe-30.5Cr-15Co-1.5Mo. Samples were annealed at each temperature for 30 min and then one sample each was quenched in water and cooled in air, respectively; b) XRD measurement of a sample annealed at 720°C for 30 min with subsequent water quenching indicating the presence of a σ-phase at elevated temperatures above the temperature of immiscibility.
temperature, which was also described by Kaneko et al. (1977) in their study. The lowest hardness was observed at 660 °C and was determined to be the temperature of immiscibility which was positively correlated with what Minowa et al. (1980) predicted for a pure Fe–Cr–Co alloy without Mo, which was a temperature of immiscibility of around 660 °C for the Mo free alloy.

Above this temperature, the hardness values appear to rise rapidly. This rise in hardness was attributed to the hardening by a sigma-phase in the material above a specific temperature. The XRD measurement of a sample annealed at 720 °C revealed the presence of this phase in the material, as can be seen in Figure 11(b). It is also consistent with a study by Cao and Zhao (2016) where the sigma-phase is predicted in a Fe–Cr–Mo system at elevated temperatures.

When using air-cooling, the hardness values stay the same above a temperature of 620 °C, suggesting a fast decomposition rate above this temperature (Cahn, 1963; Brenner et al., 1984).

The measured temperature of immiscibility was used to design heat treatment 640HT as shown in Figure 6. It is similar to the standard heat treatment applied in this material, which includes a thermomagnetic treatment 10–20 °C below the temperature of immiscibility, followed by step-wise annealing at lower temperatures, finishing at 510 °C (Bronner & Jullien, 1981; Chin, Green, Sherwood, & Wernick, 1982).

To determine the pure influence of different printing parameters on the spinodal decomposition and subsequently the magnetic properties, the first step of the heat treatment at 640 °C was performed outside a magnetic field. A second annealing treatment 510HT was performed for comparison at 510 °C and for 50 h. Hardness measurements controlled the occurrence of spinodal decomposition, as can be seen in the caption of Figure 6.

Table 2 shows the results of the magnetic measurements. Hard-magnetic properties were measured for samples 1, 2, and 4. A coercivity of around one-third to one-fourth of the value obtained for the same or similar materials annealed in a magnetic field could be achieved for these samples (Zijlstra, 1978; Homma, Okada, Minowa, & Horikoshi, 1981).

Samples #1 and #2 have a similar energy product, with #1 obtaining a slightly higher coercivity. This shows that a homogenization treatment after in-situ alloying might not be needed for a spinodal decomposition to occur and to obtain good magnetic properties. The inhomogeneity (value of inhomogeneity (Cr) for this sample equals 38) might even contribute to the enhanced coercivity due to a difference in local lattice strain and a chemical composition gradient in different regions during decomposition (Cahn, 1963; Rogström et al., 2012; Seol et al., 2003).
Samples #2 and #3 have very different magnetic properties. Sample #3 shows almost no hard-magnetic properties which can be attributed to the different heat treatments applied. The hardness values measured for both samples (452HV for #2 and 470HV for #3) suggest that in both cases a spinodal decomposition has occurred. However, as can be seen in Figure 11, decomposition above 620 °C occurs very rapidly and therefore the structures of the phases developed in both annealing treatments can be estimated to be different resulting in the different magnetic properties observed. This rapid decomposition close to the point of immiscibility has been shown to be of great importance when annealing in high magnetic fields (Cahn, 1963; Homma et al., 1981; Brenner et al., 1984). According to the results obtained in this study, it also seems to have an influence on the type of decomposition in the absence of a high magnetic field.

Samples #2 and #4 show similar magnetic properties with #4 obtaining a higher magnetic remanence while simultaneously having a similar coercivity. Additionally, a slight anisotropy (see Figure 12) and a higher stability of magnetic properties at elevated temperatures (see Figure 13) could be observed in sample #4. Figure 13 shows the results of the measurements of magnetic properties at different temperatures. For both samples, magnetic properties can be observed up to 500 °C. However, for sample #4, both coercivity $H_c$ and magnetic remanence $M_r$ seem to be more stable at elevated temperatures. Thus, it is shown that the printing parameters appear to have an influence on the magnetic properties of homogenized samples.

![Figure 12. Anisotropy observed in sample #4. The orange curve indicates the measurement parallel to and the blue curve perpendicular to the building direction in the LPBF machine.](image-url)
4. Summary and conclusion

A process for the in-situ alloying of an Fe–Cr–Co–Mo alloy using the LPBF process has been developed using melt pool and parameter studies. The influence of the printing and post-printing conditions on the magnetic properties has been demonstrated:

- Melt pool studies of elemental powder components have been shown to be partially able to predict stable parameters for the printing process when using in-situ alloying.
- Stable samples have been printed from two different powder mixtures and a correlation between powder quality and part quality in the in-situ alloyed parts has been shown.
- The influence of printing parameters on the chemical homogeneity of the in-situ alloyed samples has been investigated and a correlation between these two has been found.
- Hard-magnetic properties have been obtained for selected samples and it has been shown that these properties seem to be dependent on the process conditions applied.
- The thermal stability of the hard-magnetic properties of samples printed with different parameters has been demonstrated.

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Figure 13. Measurement of magnetic properties at different temperatures. Magnetic properties (both coercivity $H_c$, displayed in blue and magnetic remanence $M_r$, displayed in orange) seem to be more stable in sample #4(b) than in sample #2(a).
Disclosure statement

The authors declare no conflicts of interest.

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