Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

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PhD Program: MATHEMATICS AND MECHANICS

Title of Thesis: PROPERTIES AND CHARACTERISTICS OF THE CrFeCoNi HIGH-ENTROPY ALLOYS AND ITS MODIFICATIONS PRODUCED BY ADDITIVE MANUFACTURING TECHNIQUE

Supervisor: Prof. Igor Shishkovsky

Co-Supervisor: Prof. Stanislav Evlashin

The thesis document includes the following changes in answer to the external review process.

Pinaki Prasad Bhattacharjee

As the thesis is presented as a collection of published papers, I would have liked to see a more detailed section 1.6 on Applied Methods and Techniques for ease of reference.
I agree that it would be useful information. However, since for each article different equipment and parameters can be used, the decision was made to present the used technique only.

Chapter 2

1 In section 2.3, the XRD method was introduced. Kindly mention the surface from which the analysis has been carried out. Though the scholar has mentioned the top surface, it could lead to confusion; rather, mention the surface in terms of build-direction (BD) or scan-direction (SD) etc.
The clarification was added in the Intro section: “The "top" and "front" labels indicate the cross-sections perpendicular to the build-direction and scan-direction, respectively.”

2. In all the figure captions, mention the conditions properly for the ease of understanding of the readers (for example, annealing temperature, power density etc.).
Thank you for the comment. I agree that image labeling facilitates the understanding of the study. In further studies, the captions to figures were added properly.

3. Did the scholar investigate the reason behind the sharp intensity of (220) peak in XRD? If yes, do mention the origin of such phenomena. (In section 3.3).
The (110) direction is common direction observed for the fcc materials. The (100) crystal structure forms along heating flow during the crystallization of the melt pool. But, since the laser spot moves along the surface, the preferable direction (110) is forming along BD. Therefore, the scanning parameters impact the texture character in the printed material as can be for Inconel718, Fig.1.

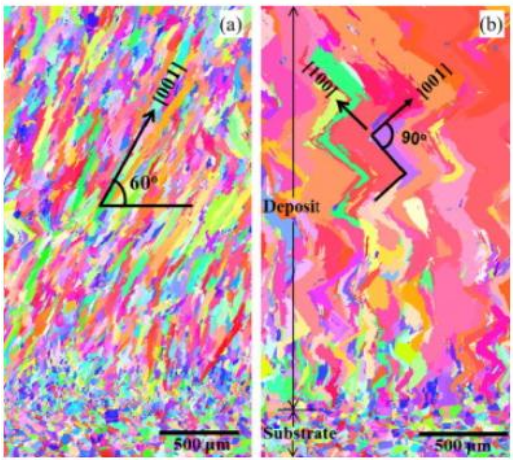


Figure 1. EBSD maps of the as-deposited IN718 for two different laser beam scanning patterns [Dinda].

[Dinda]G.P. Dinda, A.K. Dasgupta, J. Mazumder, Texture control during laser deposition of nickel-based superalloy, Scr. Mater. 67 (2012) 503–506. doi:https://doi.org/10.1016/j.scriptamat.2012.06.014.

4. In section 3.3, the Mn evaporation is mentioned without any data quantification; please add a table for the same.
The Mn evaporation was discussed for the CrFeCoNiMn alloy presented in the referenced study. In our study, we investigated the CrFeCoNi alloy, therefore the Mn evaporation was not observed.

5. In section 3.3, the decrease in lattice size is inconsistent with power density. At 800 J/mm3 the value is quite high. Is there any specific reason?
The higher value of lattice parameter for the 800 J/mm3 is associated with deviation of calculation.

6. In Fig.6, the IPF axes were not mentioned, as they were captured from different planes. Mention the parallel axis (such as BD || <100> or SD || <100> and so on). Moreover, in the Pole Figures, keep the maximum intensity the same (if possible) in all cases for easy comparison.
Thank you for the comment. The improvements of the images are not possible in the article to date. However, the comments will be taken into account for future studies.

7. In section 3.5, the discussion of mechanical properties the aspects of twining and dislocation glide are mentioned. Is there any evidence of the same, such as from the TEM images?
Unfortunately, the TEM analysis was conduct in section 3 only for structural observation and phase analysis. For the investigation of deformation mechanisms, the additional study is required.

8. As mentioned by the scholar, there is a decrease in ductility due to the formation of the sigma phase. Is there any attempt to remove or solutionize the sigma phase from the matrix in such a case? This could have prohibited the deterioration of mechanical properties.
The formation of the secondary phase is associated with the impurity of the initial powder, which cooled down in the nitrogen atmosphere during production. We assume that using the argon atmosphere may increase the purity of the powder and avoid the formation of secondary phases.

Chapter 3
1 Fig.3(a).: There seems to be a lot of variation in the error bar for hardness tests conducted at different temperatures. Why so?
The microhardness variation is associated with the bimodal structural distribution in the printed material.

2. Fig.3(b).: There is a sharp decline in hardness between 1 hour to 3 hours at 500˚C but no such

observation at 600 ˚C. Is there any explanation regarding this? Also, in the same figure, the hardness decreases when the annealing duration is increased to 500˚C. In contrast, there is a slight increase in hardness value at 600˚C when the annealing duration is increased up to 24 hours. Is there any justification for that?

Indeed more investigations are required to understand this phenomenon. Schuh et al. investigated the HPT CrFeCoNiMn alloy and observed a similar microhardness response at a lower temperature of 450C which continuously increased for 100h. They suggested several possible explanations: i) the formation of precipitates on the grain boundaries hinding dislocation emission; ii) reduction of the dislocation density upon annealing; and iii) the formation of the small secondary intermetallic phases, which were not detected at this temperature but were observed at higher temperatures, contributing to the strength.

But, the four-component CrFeCoNi system demonstrates the stable single phase at elevated temperatures (if we talk about pure material). In our case, we have a high content of nitrogen in the material resulting in nitride formations starting from 600C. But, we observed an increase in microhardness for our material for a short period of time at low temperatures. The material loses strength after one hour of annealing at 500C. At this temperature, the endometric DSC peak is observed while the microstrain value calculated through XRD patterns demonstrates slight changes up to 700C. The more precise neutron diffraction analysis (Chapter 6) demonstrates the reduction of residual stresses at 600C without observation of secondary phase formation.

To summarize, both explanations of the nature of this behaviour are arguable and it requires additional investigations. According to the data presented in Chapter 3, I am more inclined to the dislocation starvation explanation. But again, I do not have additional proof of the defect starvation point of view.

3. Section 3.2: The scholar mentioned the presence of bimodal grains, but I don't find any proper reasons behind this observation and its possible effect on mechanical properties.

Bimodal grains are typical for the PBF fcc alloys. They are forming due to the laser movement and overlapping/remelting of the neighbor laser tracks. Depending on the laser speed, the crystallization direction may be turned to the middle line of the laser track forming elongated grains, Fig.2.

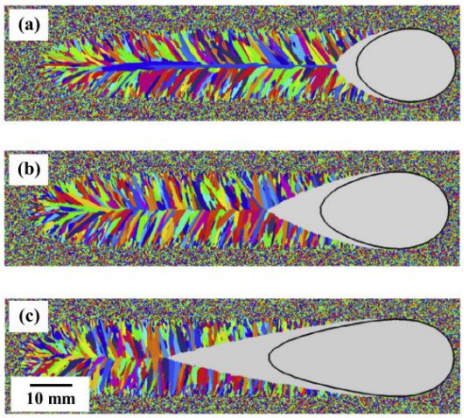


Figure 2. Effect of undercooling on the grain structure [DebRoy].
Scanning speed (a) 1 mm/s, (b) 2 mm/s, and (c) 5 mm/s.

[DebRoy] DebRoy, T., Wei, H. L., Zuback, J. S., Mukherjee, T., Elmer, J. W., Milewski, J. O., Beese, A. M., Wilson-Heid, A., De, A., & Zhang, W. (2018). Additive manufacturing of metallic components – Process, structure and properties. *Progress in Materials Science*, *92*, 112–224. https://doi.org/10.1016/j.pmatsci.2017.10.001

4. The scholar should have considered including the EBSD maps in section 3.2, which would have been very helpful to the readers in understanding the different grain sizes observed after annealing at different temperatures.

Thank you for the comment. The improvements or adding of the images are not possible in the article to date. However, the comments will be taken into account for future studies.

5. Section 3.2: In the last line of the second paragraph, the scholar mentioned the observation of high irregularity of microstructure after annealing at 700˚C and 800˚C. However, there is no discussion on possible reasons behind this.

The comprehensive discussion was in the Conclusions section:
"An in situ neutron diffraction analysis showed that 3D printing results in a high micro-strain due to high dislocation density in the CrFeCoNi alloy. Additionally, the analysis revealed the recovery process of the as-printed material at 850 K (577°C), which does not occur in the as-cast material up to 1000 K (727°C). The DSC analysis demonstrated the endothermic peak associated with recovery process beginning at temperature of 400°C with a peak maximum at 500°C, which particularly is associated with the recovery of point defects. At the same time, the neutron diffraction analysis revealed the begging of the dislocation movement at temperature of 850 K. The cellular substructure remains stable even after long heat treatment at 600°C for up to 21 days. The transmission electron microscopy revealed that the cellular microstructure degrades and coalesces after 24 hours annealing at 700°C leadgin to the drop in microhardness. The continuous recrystallization process may occur staring from the temperature of 800°C. Subsequent structural analyses of printed CrFeCoNi alloy showed dislocation-free grain growth at 1000°C, while the texture of the material remained unchanged at this temperature. Such material behavior indicates the application of the PBF CrFeCoNi alloy at elevated temperatures is limited. Only further chemical modification may increase the possible temperature application range. Although, the as-built alloy can be effective for structural applications at room temperature and below 600°C."

6. Fig.5(b,d,f) What are the small black circles/spots? Please mention it.
There are the nanoparticles or nanopores after the particles were removed during the polishing procedure. One of them was recognized as M23C6 precipitate. The similar segregations in the cell boundaries (but with different chemical composition) are observed in PBF 316l steel [Wang].

[Wang] Wang, Y. M., Voisin, T., Mckeown, J. T., Ye, J., Calta, N. P., Li, Z., Zeng, Z., Zhang, Y., Chen, W., Roehling, T. T., Ott, R. T., Santala, M. K., Depond, P. J., Matthews, M. J., Hamza, A. v, & Zhu, T. (2018). *Steels with high strength and ductility*. *17*(January). https://doi.org/10.1038/NMAT5021

7. Fig.8(a,b): Please mention the zone axis of the indexed diffraction pattern.
The clarification was added in into section: "Fig. 8. The TEM images were obtained from the sample plane transversal to the building direction."

8. The quantification (even rough calculation) of the precipitate phase fraction will be appreciable.
Roughly it can be estimated as ~1 at% of M2N phase. The maximum value of nitrogen in the initial powder ~0.1 wt% (roughly, it is 0.3 at%), so with two atoms of metal it may provide maximum of ~1 at % of secondary phase.

Chapter 4
1. Fig.3 – superimpose high angle boundary, low-angle boundary, and CSL in both the micrographs. 2. Increase the fronts of the micron markers of EBSD maps in Fig.2 and Fig.3.
Thank you for the comment. The improvements of the images are not possible in the article to date. However, the comments will be taken into account for future studies.

3. Section 3.3, shift in XRD peaks can also happen due to compositional change. Justify.
The formation of nitrides may decrease the nitrogen value in the solid solution. In turn, it may impacts the lattice parameter (or peak position).

4. The peaks for secondary phases are not visible. Put an enlarged figure. The quality of Fig.4 (c) and (d) is not very impressive. Enlarge the images and do the necessary contrast/brightness corrections.
Thank you for the comment. The improvements of the images are not possible in the article to date. However, the comments will be taken into account for future studies.

5. Fig.5 Element names are not visible properly. Enlarge them.
Thank you for the comment. The improvements of the images are not possible in the article to date.

However, the comments will be taken into account for future studies.

6. Fig.6: From which direction the tensile specimens were extracted?
Thank you for the comment. The clarification was added in into section: “The tensile and fatigue tests were conducted along the samples produced along the build direction.”

7. Although the impact of machining has been clarified, what could be the role of the dominant deformation mechanism on the fatigue strength of the additively manufactured alloy?
The corresponding discussion was added in Intro section:
“The observed deformation slips (Fig. 9a and 9b, Chapter 4) were recognized as twins similar to those observed in the CrFeCoNiMn alloy after intensive deformation [58]. However, the TEM analysis is needed to prove this statement. Additionally, Laplanche et al. indicated the critical stress of 720 MPa at which twins appear in the CrFeCoNiMn alloy at 77 K [40]. Indeed, they observed twins in the material tensile tested at room temperature after the true stress reached 820 MPa (usually, such stress is reached close to fracture) [40]. The same as Cantor’s alloy, the CrFeCoNi alloy may involve the planar slip deformation mechanism as the main at earlier stages while twinning may appear at the later deformation stages. Note that, for this study, the true stress of 800 MPa reached for the as-built and annealed materials at strains of 0.17 and 0.21, respectively (Fig. 6b, Chapter4). It may indicate the twinning observation for the as-built CrFeCoNi alloy at an earlier deformation stage. However, this discussion requires additional investigations and proof. According to the present results, it can be argued that twins are not observed in the material after cyclic loading up to 480 MPa involving the dislocation slip deformation mechanism only, while the tensile-tested samples may consist of twins, but additional analyses are needed.”

8. Section 3.6: There is a transition of deformation mechanism (twinning to slip) from tensile to cyclic loading? Please clarify in-depth.
Thank you for the comment. The discussion was added in the Intro section.
“One of the conclusions made in the study was: "The twinning deformation mechanism takes place at the tensile deformation, while dislocation slip dominates at cycling loads of 480 MPa". It is not correct in this state. The observed deformation slips (Fig. 9a and 9b, Chapter 4) were recognized as twins similar to those observed in the CrFeCoNiMn alloy after intensive deformation [58]. However, the TEM analysis is needed to prove this statement. Additionally, Laplanche et al. indicated the critical stress of 720 MPa at which twins appear in the CrFeCoNiMn alloy at 77 K [40]. Indeed, they observed twins in the material tensile tested at room temperature after the true stress reached 820 MPa (usually, such stress is reached close to fracture) [40]. The same as Cantor’s alloy, the CrFeCoNi alloy may involve the planar slip deformation mechanism as the main at earlier stages while twinning may appear at the later deformation stages. Note that, for this study, the true stress of 800 MPa reached for the as-built and annealed materials at strains of 0.17 and 0.21, respectively (Fig. 6b, Chapter4). It may indicate the twinning observation for the as-built CrFeCoNi alloy at an earlier deformation stage. However, this discussion requires additional investigations and proof. According to the present results, it can be argued that twins are not observed in the material after cyclic loading up to 480 MPa involving the dislocation slip deformation mechanism only, while the tensile-tested samples may consist of twins, but additional analyses are needed.”

9. Section 4.3: What is the solvus temperature for the σ- phase? Annealing above that temperature could’ve resolved the crack propagation issue.
The formation of sigma phase in CrFeCoNi alloy was not proved. However, the M2N phase formation was observed with BSE imaging up to 800C. The annealing at 900C leads to the small nitride particles formations observed only with TEM imaging. According the data available for the Cantor’s alloy and observation for the CrFeCoNi alloy after 1000C annealing, I suggest that at 1000C the formation of nitrides should not occur in our material.

Chapter 5
1. The AM is a net-shape process and is highly unlikely to justify severe plastic deformation processing. Therefore, the motivation for this part of the work should be justified better.
The corresponded discussion was added in the intro section:
“Further research is being conducted on AM HEA materials to explore the effects of post-treatments on their properties. One particular focus is on grain refinement, which has proven to be a successful method

for enhancing strength characteristics. Additionally, the analysis of the printed material behavior after a high load allows a better understanding of its possible application conditions as a structural material and ways of property improvement, for example, by grain refinement."

2. The AM HEA is subjected to up to 8 HPT turns, whereas the CM HEA is subjected to up to 5 HPT turns. This translates to a great difference in the overall strain. Any comment?
Performing the number of turns as ½, 1, 2, 4, and 8 allows to easily building the logarithmic plots, so from this point of view, this number of turns is more valid. The data for CM material was obtained earlier and it is extremely interesting to compare the obtained results even if the final number of turns is different. Moreover, the equivalent strain (ε) takes into account the number of turns, and the data for both materials demonstrated that the hardness saturation occurs at ε=12 in both materials while these have different processing routes that cause different initial hardness before HPT.

3. I don't see any micrograph for HPT-processed CM HEA. It would be appreciable if some micrographs were included. 4. P.2; Section 2, last paragraph: The author has mentioned that nanoindentation tests were carried out for AM and CM CoCrFeNi HEA before and after HPT, but then why are there no load-displacement curves for CM HEA before HPT in Fig.4(b)
The corresponded images and loading curves of CM HEA presented in the earlier publication of our co-authors [Zhao].

[Zhao] Zhao, Y., Wang, X., Cao, T., Han, J. K., Kawasaki, M., Jang, J. il, Han, H. N., Ramamurty, U., Wang, L., & Xue, Y. (2020). Effect of grain size on the strain rate sensitivity of CoCrFeNi high-entropy alloy. Materials Science and Engineering: A, 782. https://doi.org/10.1016/j.msea.2020.139281

5. P.3; Fig.1(b): Why does the hardness value decrease between 3.5mm to 4.5mm for HPT-processed CM HEA? Is there any reason for that?
There is a higher error for this section of the sample compared with other measurements near the center (5 turns). It can be associated with the inhomogeneity of the applied load due to technical reasons.

Chapter 7
1.Table 1: Why is there such a huge loss (nearly half) in every alloy?
There are two possible ways of aluminum loss: 1) the loss of the material during the mixing process since the aluminum softer material compared with CrFeCoNi alloy; 2) evaporation of the aluminum during the printing as it is observed for other materials such as Ti6Al4V alloy. I suggest that two processes occur. However, the effect of the evaporation is more sensitive since we varied the mixing process and still observed the same tendency.

2. Fig. 1(a) and (b): why are there such arbitrary and massive variations in porosity and hardness values for certain conditions? (For example, M0 in porosity and M3 in microhardness)
The porosity was calculated from the optical images and there are some images with higher porosity values especially for the low and high volumetric energies. It contributes to the higher error. The materials containing the aluminium demonstrated the formation of a new phase enriched with Al. The value of the formed phase is out of the limit of the XRD analysis, however, the EDX analysis and BSE images demonstrated such regions. The inhomogeneous formation of this phase may lead to higher hardness dispersion.

3. Section 3, para 2: It is unclear what those particles are rich in Al. Is this a phase rich in Al? or some segregation?
It is a phase enriched with Al (not particles) with typical for spinodal decomposition structure, Fig. 3. The point EDX analysis demonstrated up to 32 at% of Al in such regions. This number was not mentioned in the publication due to the article limit and due to the repeating the observation from the EDX map in Fig. 2h.

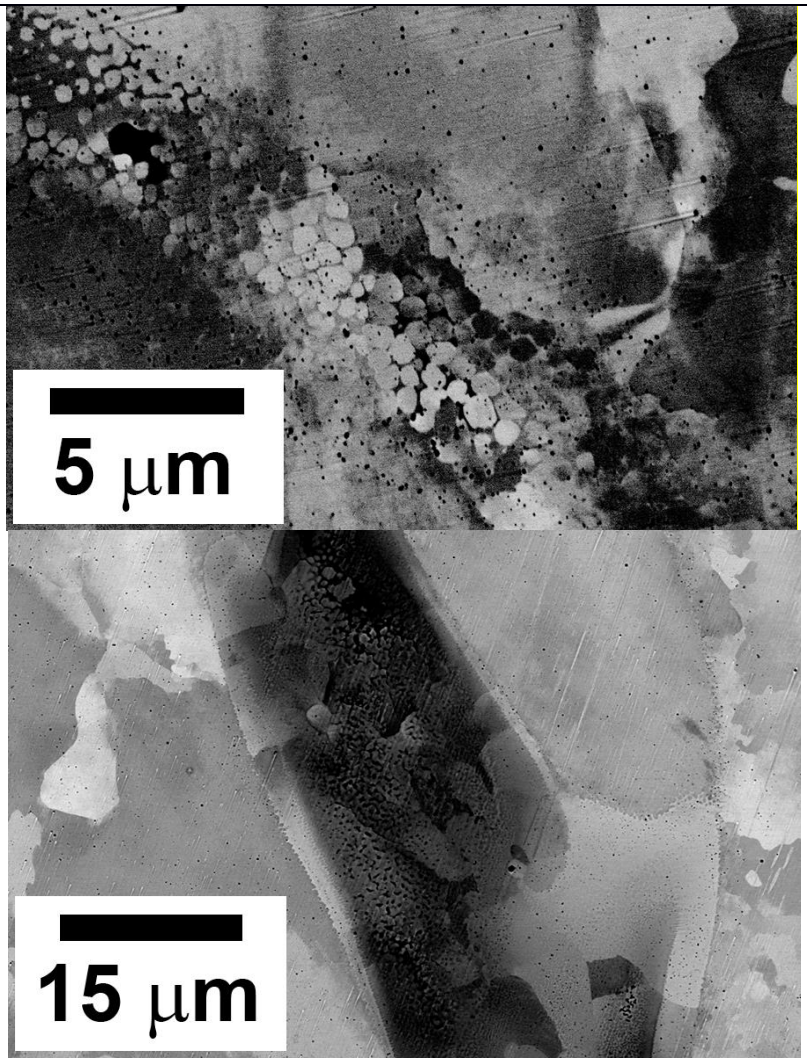


Figure 3. BSE images of the regions enriched with Al presented in the publication.

4. Fig.2: What is the volume fraction, structure, and chemical composition of the precipitates formed after annealing?

For the precise chemical composition and crystal structure recognitions, the TEM analysis is needed. Unfortunately, we don't have its results. The XRD analysis does not demonstrate any additional phases, so we can conclude that the amount of the formed precipitates is less than 5%.

Chapter 8

1 In section 3, it is mentioned that "the present study, the preliminary powder contains ~1 wt% of Mn, which can be enough for the formation of the same oxides on the surface due to the high diffusion rate of Mn (Laplanche et al., 2016)." Please mention if this originates due to the inter-diffusion or the self-diffusion phenomena.

We didn't conduct additional research on this phenomena, but we can suggest based on the results for the CrFeCoNiMn alloy (Laplanche et al., 2016) that the Mn self-diffuses to the upper oxidized layer while Cr is concentrated at the lower oxidized layer.

2. In section 3, it is mentioned regarding the possibility of the presence of a spinel phase in the A0 sample. Is there any direct evidence of the same?

We presumable the formation of the spinel phase since we observed the M3O4 peaks according to the XRD data and this phase was found for the oxidized CrFeCoNiMn alloy. The XRD data (Fig.4) was included in the Intro section of the chapter.

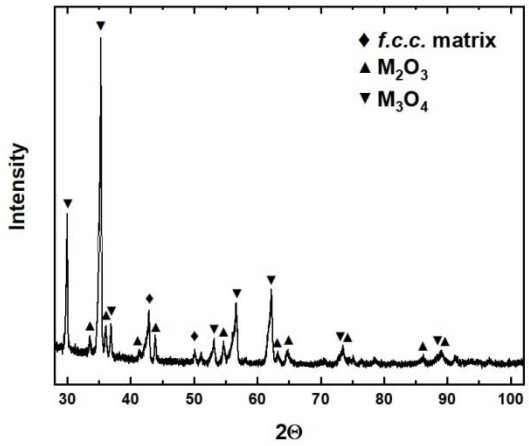


Figure 4. XRD data of A5 sample (1000 °C, 500 h), Chapter 8.

3. Section 3 (page 4) mentions that aluminum nitrides transform into aluminum oxides without appropriate experimental evidence. Please clarify.

The comparison of Gibbs free energy change for Al oxides and Al nitrides demonstrates the stability of the oxides in the wide temperature range, Fig.5. Since we see the layer enriched with nitrides going to the layer enriched with oxides, the corresponding statement was proposed. However, we agree that no experimental evidence was observed, only theoretical explanation.

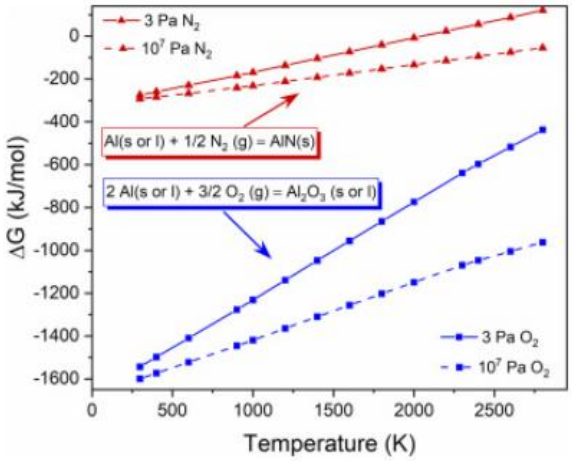


Figure 5. Comparison of Gibbs free energy change, ΔG, of the formation of Al oxide and Al nitride as a function of temperature, T, at two constant pressures [Golizadeh].

[Golizadeh] Golizadeh, M., Mendez Martin, F., Kolozsvári, S., Anders, A., & Franz, R. (2021). Cathode spot behavior in nitrogen and oxygen gaseous atmospheres and concomitant cathode surface modifications. *Surface and Coatings Technology, 421*. https://doi.org/10.1016/j.surfcoat.2021.127441

4. In Fig.4, for the A5 condition, the variation in hardness was attributed to the alternate oxide and nitride layers. It is further mentioned that the hardness is related to the oxide layer formation. The presence of an oxide layer increases hardness most of the time; however, there is also a nitride layer in this case. Hence, it is unclear whether the origin of high hardness values is related to oxide or nitride layer formation. Any comments?

The hardness near the surface relates to oxides formation which is observed up to a depth of ~80 μm. Further comparably high microhardness value (up to ~250 μm) associated with nitride formations. Possibly, there is a difference in hardness between the oxide-rich and nitride-riched layers, but it was not detected with microindentation.

5. In section 3, it is mentioned that "However, high content of Al accelerates the kinetics of the oxidation process, which is observed at 1000 °C (Fig 1d)." Is it always true that the high

aluminum content increases the kinetics of the oxidation process in HEAs? Justify this statement.
In the context of the presented study, the material with a higher content of Al accelerates the kinetics of the oxidation process. It is well seen in Fig.1d. Usually, the formation of α-alumina is considered as a prevention of oxidation in the materials with >5 wt% of Al. In our case (A5 – 3 wt% of Al), the more intensive formation of the alumina may lead to a higher weight gain compared with the A1 sample demonstrating the delamination of the oxide scale at 1000C. However, the general context takes into account the absolute aluminum value at a specific composition at a specific temperature. For example, the oxidation kinetic for FeCrAl and FeNiCrAl alloys is lower at temperature of 1050C and higher at temperature of 900C [Kim]. Additionally, the FeNiCrAl alloy with lower content of Al demonstrated higher oxidation kinetic at 900C and 1050C compared to the FeCrAl.

[Kim] Kim, C., Tang, C., Grosse, M., Maeng, Y., Jang, C., & Steinbrueck, M. (2022). Oxidation mechanism and kinetics of nuclear-grade FeCrAl alloys in the temperature range of 500–1500 °C in steam. Journal of Nuclear Materials, 564. https://doi.org/10.1016/j.jnucmat.2022.153696

Chapter 9
1 A general comment: In this case, several phases are present in the material under several conditions, such as FCC, BCC, and sigma phase. It would be more illustrative if the TEM results were included in this work, as it will add more clarity regarding the phase identification.
I absolutely agree that the TEM is needed for the clarification of the observed phases. Unfortunately, we are limited to this type of analysis at this stage of research. I hope that it will be possible to conduct the TEM analysis in future study steps.

2. The scholar did not investigate the phase fraction of sigma, which can be quite useful in predicting the high hardness value. As the presence of sigma is detected using XRD, it should also reflect in EBSD. Mention the sigma content in various conditions.
Indeed, the EBSD should identify the sigma phase and reveal its fraction. But, as can be seen from the BSE imaging, the small precipitates of the sigma phase are located intercrystalline, therefore the EBSD signal may include data from several phases. It complicates the estimation of this phase with EBSD analysis. Possibly, the longer heat treatment at 800C will lead to the formation of big enough precipitates for their easier recognition.

3. The statement, "The deformation occurs through the twinning mechanism, and the corresponding structural features are observed on the fracture surface of the 0A sample (picked image in Fig.8d)." given in tensile test properties corresponds to a fractography image. The image does not provide adequate evidence for twinning. One should consider adding a post-tensile deformed EBSD or TEM (dark field image) for better clarity of twinning-assisted deformation.
I agree. It is not correct statement. Therefore, it was rewritten:
"The slip lines crossing over the grains are well-seen for the 1A sample with the lowest Al content, Fig. 10a. They are the same as for the four- and five-component CrFeCoNi(Mn) systems [35,36]. They were recognized as twins in Cantor's alloy and observed at a later deformation stage [37]."

4. Prepare and add a table showing the formation and solutionizing temperatures of the sigma phase and grain size, as it will be easier to relate with the mechanical properties.
I agree that it would be valuable observation to present all this data in the table. However, this task required additional studies since the solutionizing temperatures of the sigma phase can be obtained with additional investigations. Since it is an important question, we will consider developing our research in this direction.

5. Finally, there are several mistakes in grammar and English in this Chapter. Please rectify these mistakes in the final version of the thesis.
Thank you for the comment. All founded mistakes were improved.

Daria Lazurenko

In the 1.4 section three types of stresses are discussed. The author writes that macro stresses can be estimated by hole-drilling method and micro- and sub-micro by X-ray or neutron diffraction, which is not completely correct. All three types of stresses can be estimated by X-ray varying a beam size; however, neutron diffraction is difficult to apply for sub-micro stresses measurement.

Thank you for the comment. The text was corrected: "All three types can be estimated using non-destructive X-ray or neutron diffraction techniques, even it is challenging to apply neutron diffraction for a sub-micro stresses measurements."

Chapter 2: Identification of phases and especially finding the lattice constants using the only one diffraction peak can't be considered reliable (as in the case of bcc FeCr and delta phase, Fig.3b). Also, no information was provided about the method of lattice parameters calculation.

I agree that the first presented conclusion about the formation of the bcc FeCr phase did not have enough proves in the manuscript. Moreover, further more comprehensive investigations did not reveal the bcc FeCr phase in the annealed CrFeCoNi alloy. The secondary M_2N phase only was observed in the fcc matrix after heat treatment at the temperature range 700-800 ^{o}C, according to the EDX and TEM diffraction analyses. The fcc lattice parameter was calculated from the peak positions at XRD pattern through the Bragg's equation.

Chapter 3: According to the information provided in the paper, the concentration of nitrogen in the material was below 0.1 wt %, however, in the introduction part "up to 1 wt % of nitrogen" is mentioned, which is quite confusing. Also, as M2N was recognized as sigma-phase in previous study, it would be more convenient if the author provides the crystal structures of both phases.

Thank you for the comment. It is a typo in the intro section. The correct value is 0.1 wt% of nitrogen as presented in the publication. The mistake was improved.

Unfortunately, due to insufficient analysis of the formed new phase, it was recognized as a sigma phase in the first publication while more comprehensive investigations in the further publications demonstrated the nitrides formation only. The additional information clarifying this misunderstanding was added to the intro sections of Chapters 2 and 3.

Chapter 5: The discussion on the micromechanical properties of AM and CM HEAs could be more convincing if the comparison of the structural evolution of both would be provided. However, the chapter is limited only by the structural analysis of AM alloy.

I agree that presenting both structures would be more informative. However, the publication consists of a reference to the study where the structure of the cast CrFeCoNi alloy with similar elemental composition was considered in detail [Zhao]. Therefore, the AM structure and the reference to the study were presented.

[Zhao] Zhao, Y., Wang, X., Cao, T., Han, J. K., Kawasaki, M., Jang, J. il, Han, H. N., Ramamurty, U., Wang, L., & Xue, Y. (2020). Effect of grain size on the strain rate sensitivity of CoCrFeNi high-entropy alloy. *Materials Science and Engineering: A*, *782*. https://doi.org/10.1016/j.msea.2020.139281

Chapter 8: In the results and discussion section, author explain the loss of Al by the mixing procedure, however, it is not clear if the elemental analysis of the mixed powder was performed due to the absence of the corresponding data. Additionally, oxidation tests are questionable. As during tests spalled oxides were not collected, the oxidation kinetics analysis can't be supposed as reliable. The standard oxidation procedure assumes testing of the samples inside crucibles and weighting the samples together with the crucibles, which prevents the loss of spallation. From the methodology section, it is not clear how tests were performed and why the other strategy was chosen. Additionally, the phase composition of the oxide scale should be approved by XRD data.

Thank you for the comment. Indeed, the standard was not mentioned. The methodology of the study was based on the GOST 6130-70 standard. However, the standard requires the investigation of comparably big samples, which we could not produce due to technical reasons. Therefore, we decided to describe in detail the applied methods of measurement. The elemental analysis of the mixed powders was not performed since the accurate measurements of the weight ratio of each powder in the blend were presented, while the analysis of the element compositions of the as-built materials was performed with the EDX technique.

About the spallation measurements. We did not create the conditions for measuring the spallation weight

since it is not necessary for the GOST 6130. However, we agree that it is valuable information and it would be interesting to analyze it. We highlighted the information in the article that obtained data was collected without spallation measurements.
The XRD analysis was made from the sample surfaces (Figure 1), it proves the conclusions made with the EDX analysis and described in the publication. Unfortunately, we were limited by the number of images in the article, so we decided not to include XRD data. It was included in the Intro section.

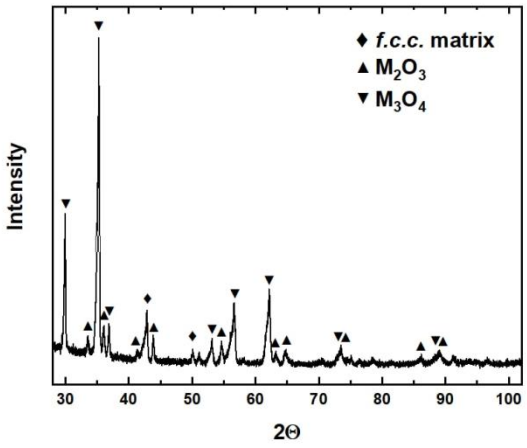


Figure 1. XRD data of A5 sample (1000 °C, 500 h), Chapter 8.

Other remarks:
Page 16: Please check if the reference to Fig. 1-1 is correct;
Page 20: author did not refer to Fig. 1-4 in the text.
Page 20: yield strength of 530 and … - measurement unit is missed.
Page 26: Cherry et al. demonstrate …. – reference is needed.
Thank you for the comments. The mistakes were improved.

Also, please revies gramma and typos, as some inaccuracies are found in the text, e.g.:
Page 14: Periodic table elements - Periodic table of elements
Page 17: Due a wide play-ground – Due to
Page 34: All these factors can results… - result
Page 40: CrfeCoNi – CrFeCoNi
Thank you for the comments. All mistakes were improved accordingly.

Tatiana Mishurova

Mrs. Kuzminova discussed a lot about residual stresses and stress relieving heat treatments. There is only qualitative proof of the heat treatment acting as stress relief. How did you make sure that the residual stress is fully relieved (for example annealed condition in Chapter 2)? Was there an attempt to measure residual stresses?

Thank you for the comment. Indeed, in our studies we made only qualitative analysis of the stress relief compared the material before and after heat treatment. Additionally, we made a test cutting the longitudinal specimens along building direction after annealing at different temperatures up to 800C. The annealed at 800C sample did not demonstrate the distortion after cutting. Of course, it is also qualitative analysis revealing the lower value of the first type residual stress only. But, for us it was enough, since the main reason of applying the heat treatment in industry is stress relief aimed prevent the distortion of printed parts (if we do not talk about phase stabilization etc.). In case of the publication presented in Chapter 2, we referenced the earlier published study [Brif]. Only the latest publication presented in Chapter 6 considers the residual stress with using in situ neutron diffraction analysis. It demonstrates the continuous decrease of the full peak width (of as-printed CrFeCoNi sample) starting from 850 to 1000 K (the measurements were stop at 1000 K due to the technical reason). These results can be interpreted as the beginning of the stress relief process begging at temperature of 850 K. BUT! These results were obtained for the cut sample, so partial stress relief occurred during the cutting. The decreasing of the peak width did not stop even at 1000 K, so we cannot say that there was a full relief of the residual stress.

Therefore, I see the task of the residual stress measurement as an important and complex research line for further AM materials development requiring the design of the thoughtful methodology and using nondestructive analytical techniques.

[Brif] Y. Brif, M. Thomas, I. Todd, The use of high-entropy alloys in additive manufacturing, Scr. Mater. 99 (2015) 93–96. doi:10.1016/j.scriptamat.2014.11.037.

The usage of powder bland showed inhomogeneous element distribution in the microstructure. Could you provide any Suggestion or how can this be improved in the future?

I would say three types of processes for this task can be distinguished:

Pre-print processes: producing the precursor powders. The required chemical composition of the powder can be achieved with mechanical alloying or use the alloy powder with similar physical properties (melting temperature, density, etc.). But, since this technique damages the powder and does not guarantee the homogeneous element distribution in the obtained powder, I would consider this technique more suitable for the DMD process rather than for the PBF requiring the high-quality morphology of the powder.

Printing: varying the printing parameters. As was discussed in the intro section, the double scanning strategy was effective for printing homogeneous CrFeCoNiMn alloy using elemental powders in the PBF process. But, in the case of printing multiphase alloys, it can be more challenging. However, we created the homogeneous multiphase alloys using elemental powders for the DMD method (will be published).

Post-printing: post-processes. At this stage, depending on the use conditions, the printed material can be processed with high-temperature heat treatments, mechanical deformation, or both.

All these techniques can be combined.

Lakshmi Narayan Ramasubramanian

1.Chapter 1. page 10. Justify the statement in Introduction: "Since it was concluded that the single-phase alloys are unlikely to meet the properties required for engineering application"
In the context, it was talking about the CrFeCoNiMn system which did not demonstrate the extraordinary properties except at cryogenic temperatures. For the high temperature application it makes sense to consider the multiple phase alloys based on this system. I agree that it can be not clear from the presented text. Therefore, this part was rewritten: "Since it was concluded that the single-phase HEAs do not guarantee the exceptional properties for engineering applications (particularly, the CrFeCoNi(Mn) system is not appropriate for the high-temperature applications) [ref], more attention was paid to the multiple-phase alloys."

2. Chapter 1. Page 11. The motivation for studying LPBF of HEAs is not clear. What is the exact need for using AM to manufacture HEAs. If there is some benefit in terms of improvement in properties or getting some other advantage, it must be mentioned by leveraging it with the disadvantages that powder production is an expensive process.
Thank you for the comment. The related info was added in the text: "This approach enables the avoidance of complex and costly prealloying procedures intended for the production of raw materials for AM. Today, plenty of works demonstrated the possibility to print HEA parts using metal powder blends. In addition to the complex geometry and unique structural characteristics provided by the AM process, tweak ing the printing parameters can yield complex multi-phase compositions in HEA, as was demonstrated for the PBF high-nitrogen steel, where the chess f.c.c.+b.c.c. phase structure was achieved by regulating laser input energy [1]."

3. Chapter 1. Page 11. "However, since the AM affects the printed material properties, the in situ AM brings more specific characteristics to the final material" These specific characteristics must be explained in few lines.
Thank you for the comment. This info was clarified: "However, since the AM affects the printed material properties, the in situ AM brings more specific characteristics to the final material such as inhomogeneous element distribution in printed material and/or printing defects related to nonoptimal printing parameters for one of the used powders."

4. Chapter 1.1. Page 13. "Jien-Wei Yeh et al. provided an intriguing explanation for investigating alloys containing five or more elements in near-equiatomic proportions". Yeh et al. is the right way to address authors.
Thank you for the comment. The mistake was improved.

5. Chapter 1.1. Page 13. The title "1.1 High-entropy Alloys. General Concepts". Better to use the title, "general concepts of high entropy alloys"
Yes. It sounds better. The subchapter was renamed accordingly.

6. Chapter 1.2. This was an excellent review of the 3 component and 5 component system and why more studies are needed in the three component, CrCoNi system. Really liked reading this.
Thank you!

7. Chapter 1.2. Page 19. It makes the CrCoNi-based alloys the most perspective materials for low-temperature applications. It should be most 'prospective' materials.
Thank you for the comment. The mistake was improved.

8. Chapter 1.2. Page 20. the addition of Ti is not discussed in detail. Is it just for forming the gamma-prime phase?
Thank you a lot for your question. I realized that there was a possible misunderstanding in the text. Ti stabilizes the bcc phase in the AlCrFeCoNiTi system which provides the main strengthening effect. The text was augmented:
"Indeed, the γ' phase was observed in the CrCoNiAl0.13Ti0.07Nb0.03 alloy after aging at 700-900°C, while at the fully recrystallized condition, this material represents the f.c.c. phase only [62]. However, the mechanical tests at elevated temperatures confirm the strength property improving at elevated temperatures, yield strength of 530 MPa and elongation of >55% at 700°C for the Al0.5CoCrFeNiTi0.15 composition

revealing the f.c.c. and b.c.c. phases [2]. The earlier study also represents the A2 Fe-Cr and B2 Al-Ni b.c.c. phases in the AlCoCrFeNiTi0.5 alloy [79]. It can be concluded that the aluminum and titanium stabilize the hard b.c.c. phase in the AlCoCrFeNiTi system which mainly contributes to the strength properties of the material."

9. Chapter 1.3. Page 22. What is the reason for higher accuracy and low roughness of builds made from LPBF?
The small laser spot diameter, the possibility to print overhanging structures, printing the support structures. This information was added in the text: "The main advantages of the process are the high accuracy of the printed parts, low roughness, and the possibility to print complex geometry, mainly provided by the small laser spot diameter and the possibility to print overhanging structures in a powder bed (or print support structures).

10. Chapter 1.3. Page 25. However, the adjusting of the alloy chemical compositions for AM looks more perspective. Prospective must be the right word here although the sentence needs grammatical revision as well.
Thank you for the comment. All mistakes were improved.

11. Chapter 1.4. (structure and texture) Page 32. "Depending on the crystal structure the easy growth directions are determined (for example, <1 0 0> for f.c.c. and b.c.c. structures, <1 0 1 0> for hexagonal-close-packed crystal structures)." The reason for why these are easy growth directions should be mentioned within the sentence itself.
Thank you for the comment. The info was added.
Depending on the crystal structure the easy growth directions are determined (for example, <1 0 0> for f.c.c. and b.c.c. structures, <1 0 -1 0> for hexagonal-close-packed crystal structures, which are the epitaxial growth directions for these crystal structures).

12. Chapter 2. Page 42. "except the yield strength values which were higher for about 300 MPa." It should be "by about 300 MPa"
Thank you for the comment. The mistake was improved.

13. Chapter 2. Intermetallics paper, page 6, Table 2. The modulus of the alloy in as printed state is 135 GPa but it increases to 205 GPa after annealing. Why is that happening?
In the present study, the required test conditions were not provided for the accurate measurements of the Young modulus (according to the standard) since it was not a goal of the study. Therefore, the qualitative Young modulus results of the study cannot be discussed. However, it is true that the tensile tests of the AM materials demonstrate the spread of the Young modulus depending on the post-heat treatment or printing conditions (printing parameters, printing direction, or better to say thermal history). In our publication presenting the PBF 316L steel, we assumed the residual stress mainly contributes to the material properties [Fedorenko]. The vertically printed samples demonstrating complex residual stress field had a 25% lower Young modulus compared with horizontal samples.

"The presence of the residual stress after the build process causes the reduction of the slope angle of the loading diagram at the initial stage of loading in comparison to the analysis of the residual stress-free specimen. In other words, the residual stress affects the measurements of Young's modulus, and the presented virtual test gives the approximate value of 150 GPa, while the experimental mean value is 158.7 GPa for the vertical specimen. The simulation under stress-free assumption gives the one used in the model, i.e. 198 GPa, which is a common result for conventionally produced steel." [Fedorenko]
[Fedorenko] Fedorenko, A., Fedulov, B., Kuzminova, Y., Evlashin, S., Staroverov, O., Tretyakov, M., Lomakin, E., & Akhatov, I. (2021). Anisotropy of mechanical properties and residual stress in additively manufactured 316l specimens. *Materials, 14*(23). https://doi.org/10.3390/ma14237176

14. Chapter 2. Intermetallics paper, page 7, Fig. 7a. The method to measure ductility in samples is not accurate. Ductility should be measured till UTS in all samples. Therefore, it is better to call it strain-to-failure. This can be mentioned in the introduction to this chapter.

Thank you for the comment. The corresponding data was added in the intro: "Due to the high ductility of the tensile tested material, the elongation at fracture measurements were conducted by the strain-to-failure method".

15. Chapter 2. Intermetallics paper, page 7, Fig. 7a. The strain hardening rates of sample tested at -150 oC and that which is printed and annealed but tested at 25 oC appear to be similar. Their ductility may vary but are the deformation mechanisms similar? Also in one case higher hardening rate leads to greater ductility wherein in the other it does not. Why is this the case? The author may need to take true stress true strain curves and check the hardening rates.

It was presented in other studies that the main deformation mechanism switches to the nanotwinning for the CrFeCoNi(Mn) alloys at cryogenic temperature [Laplanche, George]. The staking fault energy of these materials decreases with the temperature decrease which enhances twinability leading to increase in strength and ductility. In our study, we also observed the strength and ductility increases at lower temperatures for as-built material. After heat treatment, the secondary phases were observed in material. At the same time, the annealed material demonstrated the higher strength and the same ductility at cryogenic temperature compared to the properties at room temperature. This "drop" of ductility was associated with secondary phase formations.

[Laplanche] Laplanche, G., Kostka, A., Horst, O. M., Eggeler, G., & George, E. P. (2016). Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy. Acta Materialia, 118, 152–163. https://doi.org/10.1016/j.actamat.2016.07.038

[George] George, E. P., Curtin, W. A., & Tasan, C. C. (2020). High entropy alloys: A focused review of mechanical properties and deformation mechanisms. Acta Materialia, 188, 435–474. https://doi.org/https://doi.org/10.1016/j.actamat.2019.12.015

16. Chapter 3. JALCOM paper, page 3, Fig. 2, The DSC curve for powder sample appears to have a peak at 350 oC also. What is that peak?

At such low temperatures, the DSC peak is associated with the burning of moisture/pollution on the sample. Since a powder has a higher polluted surface area it was detected.

17. Chapter 3. JALCOM paper, page 9 and Fig. 11, The dislocation density values have been wrongly reported. Please note that dislocation density is generally very high. In your case you are saying it is 10-14/m2. I think it should be 1014/m2. Please mention this issue in your chapter as this appears as a typo in the figure axis label as well.

Thank you for the comment. The corresponding info was added in the intro section.

18. Chapter 3. JALCOM paper, page 9, "Annealing at 400 °C leads to an increase in dislocation density as shown in Fig. 11c, and it agrees with the thermal analysis revealing the beginning of the "recovery" peak". I did not understand this concept. Dislocation density should not increase at the early stages of recovery. At best it can remain fixed as additional density implies that the sample has increased storage of strain.

I believe that concept described in the article is not correct. Since the dislocation density was calculated from the TEM images, the calculations for the as-built and 400C annealed states (having the cellular structure consisting of the dislocation walls) have a higher error and, to date, I suppose, the dislocation density does not change with the temperature increase up to 400C. But this calculation result overlapped with DSC results; therefore the arguable conclusion was made.

19. Chapter 3. JALCOM paper, page 10, The increase in hardness with annealing at 500 oC is indeed curious. However, according to Schuh et al. it is due to the formation of secondary phases. I am not sure if the increase in strength is due to defect starvation. Is it due to the relaxation of tensile residual stresses. Were the residual stresses measured for these samples? My thoughts are influenced by Fig. 5g and 5h where the as cast and annealed samples have a similar subgrain structure. However, it would be interesting to see the sample at 500 oC and see its sub grain structure.

Indeed more investigations are required to understand this phenomenon. Schuh et al. investigated the HPT CrFeCoNiMn alloy and observed a similar microhardness response at a lower temperature of 450C which continuously increased for 100h. They suggested several possible explanations: i) the formation of precipitates on the grain boundaries hinding dislocation emission; ii) reduction of the dislocation density

upon annealing; and iii) the formation of the small secondary intermetallic phases, which were not detected at this temperature but were observed at higher temperatures, contributing to the strength.
But, the four-component CrFeCoNi system demonstrates the stable single phase at elevated temperatures (if we talk about pure material). In our case, we have a high content of nitrogen in the material resulting in nitride formations starting from 600C. But, we observed an increase in microhardness for our material for a short period of time at low temperatures. The material loses strength after one hour of annealing at 500C. At this temperature, the endometric DSC peak is observed while the microstrain value calculated through XRD patterns demonstrates slight changes up to 700C. The more precise neutron diffraction analysis (Chapter 6) demonstrates the reduction of residual stresses at 600C without observation of secondary phase formation.
To summarize, both explanations of the nature of this behaviour are arguable and it requires additional investigations. According to the data presented in Chapter 3, I am more inclined to the dislocation starvation explanation. But again, I do not have additional proof of the defect starvation point of view.
To investigate this effect, I would suggest other well-known materials, the materials without secondary phase transformations during the heating. To exclude the precipitation strengthening by secondary phase formation explanation and observe (or not) the streghing at low temperature for a short period of time.

20. Chapter 4. JALCOM paper, page 6, I observe in Fig. 7b the fatigue endurance is the same. The effect of heat treatment seems to be minimal here. On the other hand it seems exaggerated in 7a. How is heat treatment compensating for surface defects in 7a but unable to further enhance fatigue crack growth resistance in 7b.
During the cycling load, the two main processes contribute to the material damage: 1) crack formation and 2) crack propagation. In the case of the unmachined samples, the time or number of cycles is minimal since there are already near-surface defects. Therefore, in this case, the crack propagation time is essential for the fatigue life of these samples. The more ductile samples have better crack propagation resistance. In the case of the machined samples, the main contributor to the fatigue life is the crack formation process. Since the fatigue loads are higher for the machined samples, the contribution of the crack propagation life is less sensitive. Additionally, the formation of the nitrides on the grain boundaries can facilitate crack propagation which levels out the positive effect from the annealing at high cycling fatigue zone.

21. Chapter 4. JALCOM paper, page 6, in Fig. 7b, there are two additional points for the as cast and machine alloys at lower stress levels (at 400 and 300 MPa). I am not sure what they represent. Why are they marked as run-out specimens? Is there some uncertainty in the value of the fatigue endurance limit for these samples?
Typically, such a run-out marker represents that the obtained data was measured for the sample without failure (we reached the required cycling number of 10^7) [Yadollahi]. I agree that this information wasn't discussed in the text, but since the corresponding data is presented in Table 2 and in the Materials&Methods section ("The test procedure was interrupted after 10^7 cycles or sample fracture."), I prefer not to add clarification in the intro section.

[Yadollahi] Yadollahi, A., & Shamsaei, N. (2017). Additive manufacturing of fatigue resistant materials: Challenges and opportunities. *International Journal of Fatigue, 98*, 14–31. https://doi.org/10.1016/J.IJFATIGUE.2017.01.001

22. Chapter 5. Why would high pressure torsion be carried out on AM HEA? Isn't it the purpose of laser powder bed fusion to create intricate shapes with accuracy. Doing HPT would lead to distortion.
Indeed, the HPT process or other high deformation procedures lead to the distortion of the material. It makes the importance of the investigation of the AM material behaviour under such loads/processes for the understanding of their future application conditions. Additionally, as was presented in the chapter 6, the application of a deformation process (not necessarily the HPT) can be used to manipulate the residual stress in the material. The HPT samples demonstrated a lower temperature removing the residual stresses compared with as-printed material.

23. Chapter 5, MSEA paper, Page 6-7, The strain rate sensitivity of AM HEA is one order of magnitude higher than that of other fcc metals. I did not understand the reason for this observation. Can this difference be explained?
Compared to pure fcc metals, the one-order higher strain rate sensitivity is observed for the HEA itself. As was discussed in the earlier publication [Zhao], the higher strain rate sensitivity for HEA is associated with

differences in the atomic-level structure:
"In conventional fcc metals, the rate-limiting deformation mechanism is dislocation forest cutting, corresponding to activation volume (V*) values in the range of ~100–1000b^3. Fcc HEAs show much less V* values (mostly at the magnitude of ~10b^3), suggesting that the short-range barriers, which are responsible for thermal-activated deformation, are enhanced. This is because HEAs possess high lattice friction stress, resulting in much stronger Peierls barrier to dislocation motion than conventional fcc metals. In addition, it has been proved that chemical short-range ordering occurs in the atomic structure of HEAs. Such ordering is also responsible for the high friction stress in the HEAs and thus contributes to the thermal activated process, or more specifically, reducing the V* in the HEAs."

[Zhao] Zhao, Y., Wang, X., Cao, T., Han, J. K., Kawasaki, M., Jang, J. il, Han, H. N., Ramamurty, U., Wang, L., & Xue, Y. (2020). Effect of grain size on the strain rate sensitivity of CoCrFeNi high-entropy alloy. *Materials Science and Engineering: A, 782*. https://doi.org/10.1016/j.msea.2020.139281

24. Chapter 7, Materials letters paper, why does Al addition lead to grain refinement in HEA?
The aluminum atoms, as impurity atoms, slow down the migration of the grain boundaries during the recrystallization process requiring the higher energy for the further migration of the grain boundaries. It leads to the stabilization of the structure with lower grain size.

25. Chapter 8, Micron paper, It appear Al nitride is an important product in corrosion. Which element is likely to oxidize once Al is depleted. Also, does the weight gain attain a plateau with increasing time?
The main oxidized element was chromium. We observed the Cr- and O-riched top layer. Under the oxidized layer, we saw Al- and O-riched precipitates. Therefore, even with lower-than-expected Al content in the as-built material, the formation of alumina occurred.
As for gaining the plateau, it is a tricky question. On one side, yes, since the penetration of the oxygen in the material will stop due to the formation of the oxides (if we talk about the A5 sample). On the other hand, as we observed for the A1 sample, the delamination of the top oxidized layers can occur. If we do not take into account the weight of delaminated material, the weight gain reaches a plateau at some moment and even may go down. But, as was mentioned in the last comment from Prof.Lazurenko, it is better to measure the delaminated material also. In this case, the weight gain curve will be determined by two competing processes: i) losing weight by delamination, and ii) gaining weight by the oxidation continuing.

26. Chapter 9, Why does 4TiAl sample have such low ductility?
It is associated with a higher volume of the bcc phase (compared with A0, A1, and 3A samples) having lower ductility and initiating the crack formations in the material during the printing. The text was extended with microscopy analysis of the near-fracture microstructure.

27. My heartiest congratulations to Ms. Yulia and her supervisors for creating this wonderful work.
Thank you. I really appreciate by your evaluation of the work.

Ivan Sergeichev

How do you explain the different results for the recrystallization process of AM HEA discussed in Chapters 3 and 6?

Indeed, the some obtained results are controversial due to the used analytical techniques and applied conditions. The general conclusion about the recrystallization process was clarified in the Conclusions:

"An in situ neutron diffraction analysis showed that 3D printing results in a high micro-strain due to high dislocation density in the CrFeCoNi alloy. Additionally, the analysis revealed the recovery process of the as-printed material at 850 K (577°C), which does not occur in the as-cast material up to 1000 K (727°C). The DSC analysis demonstrated the endothermic peak associated with recovery process beginning at temperature of 400°C with a peak maximum at 500°C, which particularly is associated with the recovery of point defects. At the same time, the neutron diffraction analysis revealed the begging of the dislocation movement at temperature of 850 K. The cellular substructure remains stable even after long heat treatment at 600°C for up to 21 days. The transmission electron microscopy revealed that the cellular microstructure degrades and coalesces after 24 hours annealing at 700°C leadgin to the drop in microhardness. The continuous recrystallization process may occur staring from the temperature of 800°C. Subsequent structural analyses of printed CrFeCoNi alloy showed dislocation-free grain growth at 1000°C, while the texture of the material remained unchanged at this temperature. Such material behavior indicates the application of the PBF CrFeCoNi alloy at elevated temperatures is limited. Only further chemical modification may increase the possible temperature application range. Although, the as-built alloy can be effective for structural applications at room temperature and below 600°C."

What happens with Ti addition in the material since such significant changes in mechanical properties are observed?

The Ti stabilizes the hard bcc phase contributing to the strength properties of the alloy. According to the EBSD and XRD analyses, the higher value of the bcc phase can be indicated for the Ti-contained material. However, the higher volume of hot cracks is observed for the same material dramatically decreasing the elongation property of the same material.

Except for the heat treatment application, are there any other ways to improve the element distribution in the PBF material printed with powder blends?

Yes, there are several techniques that can be suitable depending on the element compositions and use conditions: mechanical alloying of the powders, varying printing parameters, and mechanical deformation of the printed material. Each of these techniques has its own advantages and disadvantages and was successfully applied to particular materials.

The thesis contains some typos and grammar mistakes.

Thank you for the comment. All founded mistakes were improved.

Sergey Zherebtsov

Title. "PROPERTIES AND CHARACTERISTICS" What the difference? I would say characteristics may include properties, but in general those are nearly the same.
I would say that by adding the "characteristics" word in the title I provide my opinion about the obtained properties through their comparison and discussion.

PROPERTIES are basic (or essential) elements or attributes, owned or possessed by something. Usually, the properties are concrete, intrinsic and objective.
CHARACTERISTICS are prominent aspects, qualities or features of something. Normally these are extrinsic and subjective.
Example: the elongation of up to 1 % is a property; "brittle" is a characteristic.

Page 11: "with/or without further intensive deformation process" Not clear. Why intensive (not usual for a start)? Please specify.
Thank you for the comment. The main idea that the alloys were produced through the conventional production line (for example, "arc melting - homogenization – hot rolling"). I agree that the intensive process absolutely is not a key. This part was rewritten: "The discussed above alloys were produced by conventional techniques such as cast alloying or arc alloying with further treatments."

What is "in situ AM"? Why metal powder blend is cheaper? Is it about powder of pure elements? Please clarify.
The definition *in situ AM* was clarified in the text: "In this work, the in situ AM is considered as the in situ alloying process assisted using AM technologies. It assumes the creation of the solid material the chemical composition of which is formed during the printing in the melting pool as a reaction between feedstock materials [32]. Such the definition does not limit the use the elemental powders only but also considers the use of the alloyed powders. This approach enables the avoidance of complex and costly prealloying procedures intended for the production of raw materials for AM."

Page 12: Why HPT? Why not usual rolling or compression?
The chapter 5 is considering the choice of the HPT. To indicate that this information will be presented below in the text, the following phrase was added:

In Intro: "…printed alloys after the high-pressure torsion (HPT) process (in chapter 5, the choice of the HPT process is discussed."
In Ch.5: "For this study, the HPT method was chosen as the most suitable option due to its ability to maintain the sample shape and easily achieve high deformations without damaging the material having comparably low ductility."

"conventional hot-rolled process" Of what? Cast condition?
Thank you for the comment. The process was clarified: "…the conventional process (arc-melting → 1000°C homogenization → hot-rolling at 1000°C with the total reduction in thickness of 92%)…"

Chapter 2. "CrFeCoNi medium-entropy alloys" In the dissertation title this alloy defirned as "high-entropy alloy"
According to the first published definition, it is a medium-entropy alloy. However, both titles of this alloy (high- and medium-entropy) are widely used in literature. I believe the "high-entropy" adjective provides a better understanding of the topic discussed in the thesis without making an accent on the entropy calculations.

Chapter 3. P 31. "sub-cell" cell structure is a sub-structure itself
Thank you for the comment. The mistake was improved.

Chapter 4. P 2 in the article. "…water quenching to remove the residual stress" Normally water quenching can result in the appearance of residual stresses...
The residual stress was removed with heat treatment which preceded the water quenching. Indeed, the water quenching provides residual stress but its level is not comparable with as-build material stress. The water quenching was chosen to minimize the secondary phase formation.

P 2 in the article. "further, "machined samples". Parameters of the processing, roughness of the surface?
This information was presented in the 3.1 Results. Consolidation section:
"The roughness of the AM-built MEA samples was 4.6 μm (Ra) and 26.2 μm (Rz) from the front surfaces. After machining and polishing procedures, it did not exceed 0.4 μm and 1.9 μm, for Ra and Rz, respectively."

P 3. "shows twins-like grains". Are these twins or just elongated grains?
To date, I think these are elongated grains. However, the TEM analysis is needed to prove one of these statements.

"exhibits a removal of the residual stress". How misorientation can show the precence (or absence) of residual stresses?
Indeed, the misorientation map results cannot guarantee the residual stress presence or absence in the material on their own. However, in the context of comparing the same material before and after heat treatment it can indirectly provide the qualitative estimation of the residual stress in these two materials considering the residual stress can be a results of the crystal structure distortion (or misorientation in the crystal) forming during fast cooling.
I agree that the conclusion about the stress removing is too arguable. It would be better to say "Comparison of the misorientation of grains in the as-built CrFeCoNi alloy (Fig. 2g [14]) and the annealed alloy (Fig. 2h) exhibits a lower residual stress level for the last...".

P 10. "The twinning deformation mechanism takes place at the tensile deformation, while dislocation slip dominates at cycling loads of ~480 MPa." I do not see any evidents of this conclusion.
Unfortunately for myself, I must agree that this state at present version is really not justified. I added the discussion in the intro section.
"One of the conclusions made in the study was: "The twinning deformation mechanism takes place at the tensile deformation, while dislocation slip dominates at cycling loads of 480 MPa". It is not correct in this state. The observed deformation slips (Fig. 9a and 9b, Chapter 4) were recognized as twins similar to those observed in the CrFeCoNiMn alloy after intensive deformation [58]. However, the TEM analysis is needed to prove this statement. Additionally, Laplanche et al. indicated the critical stress of 720 MPa at which twins appear in the CrFeCoNiMn alloy at 77 K [40]. Indeed, they observed twins in the material tensile tested at room temperature after the true stress reached 820 MPa (usually, such stress is reached close to fracture) [40]. The same as Cantor's alloy, the CrFeCoNi alloy may involve the planar slip deformation mechanism as the main at earlier stages while twinning may appear at the later deformation stages. Note that, for this study, the true stress of 800 MPa reached for the as-built and annealed materials at strains of 0.17 and 0.21, respectively (Fig. 6b, Chapter4). It may indicate the twinning observation for the as-built CrFeCoNi alloy at an earlier deformation stage. However, this discussion requires additional investigations and proof. According to the present results, it can be argued that twins are not observed in the material after cyclic loading up to 480 MPa involving the dislocation slip deformation mechanism only, while the tensile-tested samples may consist of twins, but additional analyses are needed."

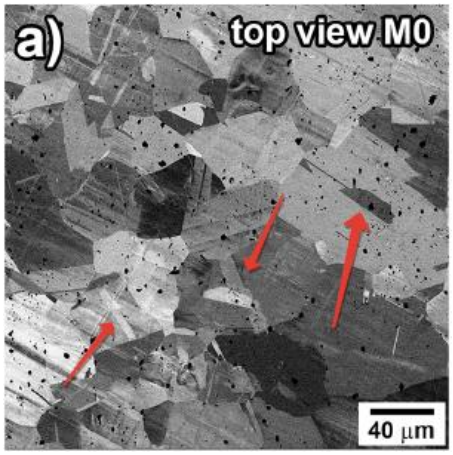
Chapter 5. P 78. "nanostructured materials". Why nanostructured? why not just fine-grained?
Thank you for the comment. I agree, the "fine-grained" is more correct. It was improved.

Chapter 3. P 9 in the article. What type of recrystallization (continuous or discontinuous)? Why recrystallization does not result in microstructure refinemen, decrease in dislocation density and the texture weakening? & Chapter 6. Summary and Conclusions. How these results are related to the above results on the effect of recrystallization?
Indeed, the some obtained results are controversial due to the used analytical techniques and applied conditions. However, the conclusion about the temperature of the begging of recrystallization process in earlier study was not accurate. It was additionally highlighted with additional discussion in Intro section (Ch.3):
"The heat treatments at temperatures lower than 700C do not provide the significant structural changes according to the microscopy observation. The presented in the article conclusion about the temperature range of the recrystallization begging of 600-700C was not accurate. Based on the in-situ neutron diffraction

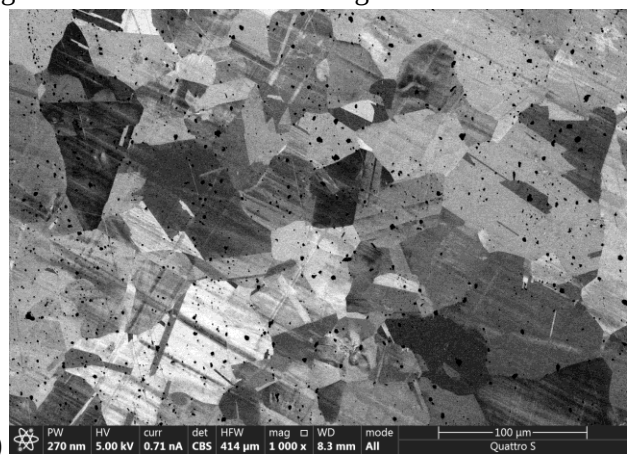
analysis results presented in the Chapter 6 it is possible to clarify the temperature range of the beginning of the recrystallization process for the PBF CrFeCoNi alloy as about 800C. At temperature of 700C the coalescence of the cell structure is seen according to the TEM observation. It can be associated with a discontinuous recovery process since the nonuniform grains are observed with the BSE imaging. After annealing at temperature of 800C and above, the small grains can be recognized as new in the BSE images which can be associated with the continuous recrystallization process. However, to clearly recognize the occurred processes, the additional investigations are required since it is challenging in some cases distinguish recovery and recrystallization processes overlapping at some temperatures."

Chapter 7. P 3. "the annealing twins". Where? How were they determined?

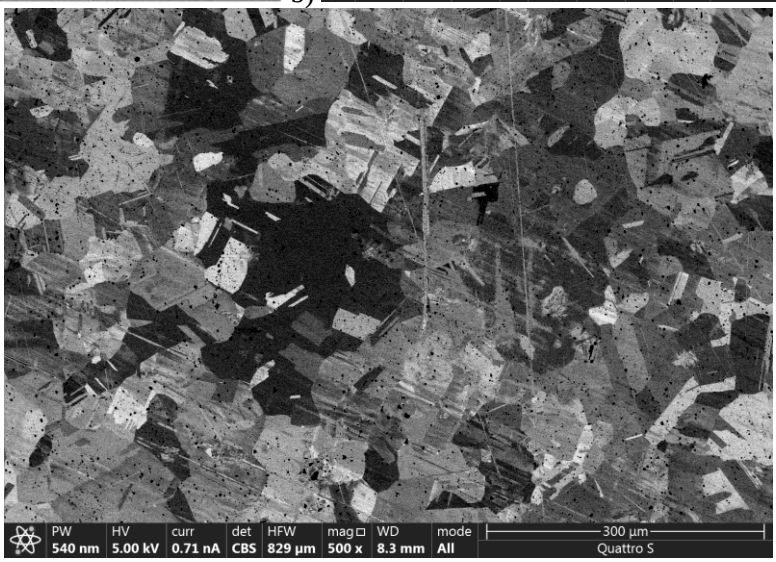
The annealing twins were visually determined (Figure 1). I understand that it is not enough to say that it is exactly the annealing twins by the visual observation. TEM analysis can be helpful in such task. However, the microstructure of M0 material significantly changed after 1200°C high-temperature annealing revealing the typical twin-like structural features. Additionally, the annealing twins were observed for the alloy having similar chemical composition after annealing at 900°C for 1 hour [Gali]. Plus, annealing twins are typically observed for the materials with low SFE and it is well-known that CrFeCoNi alloy has a low SFE [George]. Due to these reasons, it was concluded that the Fig.3a demonstrates the annealing twins.



a)



b)



c)

Figure 1. a) the BSE image from Chapter 7. Fig.3.; b) and c) the original BSE images of the M0 material after 1200°C annealing at different magnifications.

[Gali] A. Gali, E.P. George, Tensile properties of high- and medium-entropy alloys, Intermetallics. 39 (2013) 74–78. doi:10.1016/j.intermet.2013.03.018.

[George] George, E. P., Curtin, W. A., & Tasan, C. C. (2020). High entropy alloys: A focused review of mechanical properties and deformation mechanisms. *Acta Materialia*, *188*, 435–474. https://doi.org/https://doi.org/10.1016/j.actamat.2019.12.015

Conclusion. "At the as-built state, the ultimate strength characteristics are equivalent to hot-rolled materials and the yield strength properties are even higher." Since the chemical compositions are not the same, may be it is not quite correct to compare these two conditions in the dissertation conclusion.
The chemical compositions are not the same but similar (hot-rolled $Cr_{24}Fe_{25}Co_{26}Ni_{25}$ (at%) alloy in [Gali], the as-built $Cr_{24}Fe_{25}Co_{26}Ni_{25}$ (at%) alloy in the thesis). I believe these two compositions can be counted as the same and the effect of the manufacturing technique can be discussed.

[Gali] A. Gali, E.P. George, Tensile properties of high- and medium-entropy alloys, Intermetallics. 39 (2013) 74–78. doi:10.1016/j.intermet.2013.03.018.

Please, check the grammar and typos. Some of them were highlighted in the thesis text sent to you through your supervisor.
Thank you for the comments. All marked mistakes were improved.