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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Yulia Kuzminova

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: Associate Professor Igor Shishkovsky
Co-supervisor: Assistant Professor Stanislav Evlashin

Name of the Reviewer: Professor Pinaki Prasad Bhattacharjee

I confirm the absence of any conflict of interest	**09/21/2023** **Date: DD-MM-YYYY**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The PhD thesis titled “PROPERTIES AND CHARACTERISTICS OF THE CrFeCoNi HIGH-ENTROPY ALLOYS AND ITS MODIFICATIONS PRODUCED BY ADDITIVE MANUFACTURING TECHNIQUE” is an interesting attempt to understand the microstructure and properties of AM processed High Entropy Alloys (HEAs), which are materials of high importance for future structural applications.

The candidate has studied the related aspects in the papers published in good-quality journals from the research work.

Overall, the content of the thesis is sufficient and of high quality. Hence, the thesis should be considered for awarding a Ph.D. degree.

The specific comments on different chapters can be found below.

Chapter-1

The candidate has effectively introduced the relevant aspects of the thesis, including the concepts and related developments in HEAs and AM.

However, 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.

Chapter-2

In this Chapter, the scholar has studied the effect of parametric variation in the PBF method on the microstructure and mechanical properties. The study shows the effect of power density and the formation of the sigma phase playing a crucial role in mechanical properties. The present study is quite elucidating and systematic from a scientific perspective. However, several factors can improve the quality of the thesis mentioned below.

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.

In all the figure captions, mention the conditions properly for the ease of understanding of the readers (for example, annealing temperature, power density etc.).

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).

In section 3.3, the Mn evaporation is mentioned without any data quantification; please add a table for the same.

In section 3.3, the decrease in lattice size is inconsistent with power density. At 800 J/mm^3 the value is quite high. Is there any specific reason?

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.

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?

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.

Chapter-3

In this Chapter, the scholar has carried out a systematic study on the effect of heat treatment on the microstructural and phase evolution of AM-processed CrFeCoNi HEA. In this study, heat treatment is carried out at different temperatures ranging from 400˚C to 1000 ˚C for 24 hours, which results in microstructural changes, and the results are further correlated with the mechanical properties of the HEA annealed at different temperatures. The thorough study carried

out at different temperatures is appreciated. The following comments may be considered.

Fig.3(a).: There seems to be a lot of variation in the error bar for hardness tests conducted at different temperatures. Why so?

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?

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.

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.

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.

Fig.5(b,d,f) What are the small black circles/spots? Please mention it.

Fig.8(a,b): Please mention the zone axis of the indexed diffraction pattern.

The quantification (even rough calculation) of the precipitate phase fraction will be appreciable.

Chapter-4:

In this Chapter, the scholar has investigated the fatigue behavior of medium-entropy CoCrFeNi alloy synthesized by additive manufacturing. The fatigue mechanism is dominated by slip motion rather than twinning, and fatigue strength improved after removing surface defects. I appreciate the work done by the researcher, but some points are yet to be answered.

Fig.3 – superimpose high angle boundary, low-angle boundary, and CSL in both the micrographs.

Increase the fronts of the micron markers of EBSD maps in Fig.2 and Fig.3.

Section 3.3, shift in XRD peaks can also happen due to compositional change. Justify.

The peaks for secondary phases are not visible. Put an enlarged figure. The quality of Fig.4 (c) ar is not very impressive. Enlarge the images and do the necessary contrast/brightness corrections.

Fig.5 Element names are not visible properly. Enlarge them.

Fig.6: From which direction the tensile specimens were extracted?

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?

Section 3.6: There is a transition of deformation mechanism (twinning to slip) from tensile to cyclic loading? Please clarify in-depth.

Section 4.3: What is the solvus temperature for the σ- phase? Annealing above that temperature could've resolved the crack propagation issue.

Chapter 5

This Chapter focuses on the effect of grain refinement on micro-mechanical properties in

severely deformed CoCrFeNi through high-pressure torsion (HPT). This study compares microhardness and nanoindentation tests between additive-manufactured (AM) and conventionally-manufactured (CM) CoCrFeNi HEA subjected to HPT. The study showed that HPT-processed AM HEA has higher strain rate sensitivity, thus high plasticity, than the CM HEA.

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 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?

I don't see any micrograph for HPT-processed CM HEA. It would be appreciable if some micrographs were included.

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)

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?

As mentioned in this study, the micro-mechanical properties were examined at the disk edges of AM and CM CoCrFeNi HEA; however, it would have been very interesting if the nanoindentation tests were conducted from center to edge of the specimens and a result of the same could have been plotted to see the nano-hardness variation as a function of increasing distance from the center of the specimen.

Chapter-6

This Chapter is well presented. The results and the analysis are largely consistent. I do not have any specific comments.

Chapter-7

In this Chapter, the researcher dealt with the effect of low-Al content on various microstructural parameters of CoCrFeNi alloy prepared by additive manufacturing. Some comments and clarifications are listed below.

Table 1: Why is there such a huge loss (nearly half) in every alloy?

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)

Section 3, para 2: It is unclear what those particles are rich in Al. Is this a phase rich in Al? or some segregation?

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

Chapter-8

In this Chapter, the scholar has studied the oxidation behavior of CoCrFeNi HEA with different aluminum additions. This study also highlights the effect of aluminum addition, grain boundary, and constituent alloying elements affecting the nature of oxide layer formation. Though the study is thorough and interesting, I have several suggestions below.

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.

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?

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

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?

In section 3, it is mentioned that "However, high content of Al accelerates the kinetics of the oxidation process, which is observed at 1000 ℃ (Fig 1d)." Is it always true that the high aluminum content increases the kinetics of the oxidation process in HEAs? Justify this statement.

Chapter-9

This Chapter extensively discussed the phase formation and mechanical properties of PBF-processed CrFeCoNi(Al, Ti) HEA. Following are the reviews regarding the same.

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.

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.

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.

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.

Finally, there are several mistakes in grammar and English in this Chapter. Please rectify these mistakes in the final version of the thesis.

Overall, this is a very commendable research work.

I convey my best wishes to the candidate!

Provisional Recommendation

☑ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*