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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: Lakshmi Narayan Ramasubramanian

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 09-08-2023**

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 thesis written by Ms. Yulia Kuzminova is an excellent work in the field of additively manufactured high entropy alloys and provides a wealth of knowledge in terms of the strategies to develop HEAs using LPBF. The most impressive part of the work is that the student has spent a considerable amount of time in fabricating the samples (for which one can only imagine the time spent in the laboratory), and subsequently characterizing the resultant builds. Also, several aspects of the AMed HEAs were investigated and the thesis embodies a solid effort by the student to accomplish her goals of gaining a good understanding of HEAs. I personally found the structure nice but was unable to comprehend the need for chapters 5 and 6 as it digresses a bit from the goal of producing HEAs via AM. Nevertheless, the publications in these chapters are also of high quality and provide some input on what would happen if the grain structure is refined by some means (HPT in this case). The author has also made a sincere effort to connect the themes in all chapters with a detailed introduction. This provides context for whatever follows in her 8 chapters of work. The methods used in the dissertation are certainly cutting edge and strikes a chord with the sustained effort in investigating AM of HEAs and the possibilities thereof in current academic circles. Also, considering the lack of knowledge on AM of HEAs, Yulia has done a wonderful job in trying to understand and analyze data from a scientific point of view. From her dissertation it is clear that HEAs have a great potential in some critical applications and can often be better than its conventionally manufactured counterpart. Therefore, it has industrial relevance apart from generating scientific intrigue. The quality of publications is good and commendable as all of them are in Q1 journals. It is also suggested that Yulia should try her luck with more prestigious journals in future. While I wholeheartedly endorse this thesis, I do have some important comments, which the student can address in her viva and thesis. She need not resubmit her thesis and the defence can be scheduled as per the wishes of her advisor.

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”

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.

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.

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.

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”

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.

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.

8. Chapter 1.2. Page 20. the addition of Ti is not discussed in detail. Is it just for forming the gamma-prime phase?

9. Chapter 1.3. Page 22. What is the reason for higher accuracy and low roughness of builds made from LPBF?

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.

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.

12. Chapter 2. Page 42. "except the yield strength values which were higher for about 300 MPa." It should be "by about 300 MPa"

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?

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.

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.

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?

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 $10^{-14}/m^2$. I think it should be $10^{14}/m^2$. Please mention this issue in your chapter as this appears as a typo in the figure axis label as well.

18. Chapter 3. JALCOM paper, page 9, "Annealing at 400 ℃ 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.

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.

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.

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?

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.

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?

24. Chapter 7, Materials letters paper, why does Al addition lead to grain refinement in HEA?

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?

26. Chapter 9, Why does 4TiAl sample have such low ductility?

27. My heartiest congratulations to Ms. Yulia and her supervisors for creating this wonderful work.

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*