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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: Dr. Daria V. Lazurenko

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 01.09.2023**

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

Brief evaluation of the thesis quality and overall structure of the dissertation.

The thesis is devoted to the detailed analysis of high-entropy alloys produced by additive manufacturing. The topic of the study has an extremely high actuality since additive manufacturing became very important for industry. High-entropy alloys are relatively new materials (but already quite well investigated), with potential for industrial application. The majority of studies available today are focused on high-entropy alloys produced by conventional methods. For this reason, the detailed and systematic study of HEAs produced by AM techniques is of great importance.

In this study, the CrFeCoNi alloy as well as the same alloy with minor additions of Al (Al+Ti) were used as the objects of investigations. Thesis consists of 10 chapters, the first of which is introduction that contains the state of the art. In chapters 2-6, the author analyzes the four-component alloy in detail. In Chapter 2, the parameters of the powder bed fusion process used for production of CrFeCoNi were optimized. The following chapters are devoted to the analysis of influence of thermal and mechanical treatments on the

structure and properties of the alloy. In Chapter 3, the author applied different heat treatment regimes that varied the temperature and duration of post-printing annealing to analyse the structural and phase evolution. Chapter 4 contains the results of the tensile and fatigue tests of the alloy in the as-built and heat treated state. Additionally, the author provides the important information on the influence of the machining on the fatigue properties, which is useful for further commercial application of the alloy produced by BFP technique. The next step was to evaluate the structure and micromechanical properties of the alloy subjected to severe plastic deformation. The results presented in Chapter 5 evidence that the alloy produced by AM is more prone to strain hardening and possesses higher ductility compared to the alloy produced conventionally. Special attention should be paid to the results presented in Chapter 6. Using the powerful method of neutron diffraction, the author fully analysed the processes occurring at heating of as-built samples and materials subjected to high-pressure torsion. The next two chapters (7 and 8) concerns the minor additions of Al to four-component alloy and influence of Al to the structure, phase composition and oxidation resistance. Chapter 9 is devoted to the alloy dopped with Al and Ti. The author analyses the influence of the aforementioned additions on the structure and properties of the alloy in the as-built and heat treated states. In Chapter 10 conclusions and outlooks are provided. Also, the thesis contains information about publications and conferences, abstract, and bibliography.

Summing up, the thesis is of good quality, well-written, and well-structured. The author demonstrates a good understanding of the problems in the research field and working knowledge of methods and analysis.

The relevance of the topic of dissertation work to its actual content

The title of the thesis is relevant to the content.

The relevance of the methods used in the dissertation

The methods used for the investigations are completely relevant to the objectives of the study. For structural analysis, the author uses a full range of tools, including scanning electron microscopy, EBSD analysis, transmission electron microscopy, diffraction methods including in-situ neutron diffraction. The application of these methods allows for a comprehensive analysis of the structural evolution of the material induced by different external impacts. The applied methods for estimating properties are adequate and quite enough to understand the behavior of structural materials.

The scientific significance of the results obtained and their compliance with the international level and current state of the art

The dissertation represents a systematic study of the structure and properties of high-entropy alloys as materials for additive manufacturing. The study evidences the advantages of this technology application for producing HEAs from a properties point of view. In-depth structural investigations provide important information on the particularities of CrFeCoNi-based alloy formation by PBE technique and explanation of their behaviour under heating, tensile, fatigue and high-pressure torsion loads. This work makes a significant contribution to understanding both the structure-property relationship of HEAs and the

influence of production methods on these characteristics. The high-quality and approved results presented in the thesis correspond to international level.

The relevance of the obtained results to applications (if applicable)

Both additive manufacturing and high-entropy alloys are relatively new phenomena that require continuous investigations and new data. However, while AM technologies are already widely used in industry, HEAs are mainly in the investigation stage and their production by AM does indeed require further studies. This work makes a good contribution to adaptation of HEAs for industry, and particularly for the new production methods.

The quality of publications

The quality of publications is very high, and all of them correspond to international level. The results were published at 7 peer-review journals with high impact-factors indexed by Scopus and Web of Science and 1 was submitted to Intermetallics. These journals are well-known and recognised by materials science society, for this reason, the quality of the results is beyond dispute.

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

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.

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

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. Furthermore, since M_2N was recognised as sigma-phase in previous study, it would be more convenient if the author provided the crystal structures of both phases.

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

Chapter 8: In the results and discussion section, the author explains the loss of Al by the mixing procedure. However, it is known that Al can evaporate during AM. The explanation provided in the chapter should be approved, e.g. by the elemental analysis of the mixed powder before AM. 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 the crucibles and weighting of the samples together with the crucibles, which prevents the loss of spallation. In the methodology section, it is not clear how the tests were performed and why the other strategy was chosen. Additionally, the phase composition of the oxide scale should be approved by XRD data.

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.

Page 148 is empty.

Also, pay attention to grama 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

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*