COATINGS OF $Co_XCrFeMoNi$ HIGH ENTROPY ALLOY PRODUCED BY ELECTRO SPARK DEPOSITION TECHNIQUE

Laura Elena GEAMBAZU[1]*, Robert CIOCOIU[2], Florin MICULESCU[3], Ioana CSAKI[4]

This paper is focused on producing a coating for the in work components of geothermal power plants, where the aggressive environment leads to high corrosion and erosion effects. For this matter a high entropy alloy was developed, with equimolar composition. Initial tests were performed for $Co_xCrFeMoNi$ high entropy alloy produced by liquid state processing. The alloy was tested in situ, in a geothermal power plant. Material performance and the promising results are the main reason of this study. The target is to produce high entropy alloys by solid state processing and deposit them on various materials, as alternative and more economical solution for the current ones.

Keywords: geothermal, high entropy alloys, coatings, solid state

1. Introduction

The geothermal energy gathered more attention over the years, due to the fact that this renewable energy can supply electric and thermic resources for the end users at minimum costs, but also for being an environmental friendly type of process. The main concern in this type of environment is represented by the corrosion-erosion effect, due to the aggressive media, where the chemical composition of the steam and other geothermal fluids are mainly composed of H_2S, CO_2 and CH_4, with high temperatures and pressure and other factors as abrasive particles that collide with the surfaces with high velocity.

Therefore, research has been focused on developing a material, resistant to the aggressive factors that damage the in work components of the power plants.

For this matter, the high entropy alloys are the subject of multiple studies [1-7] and represent the main focus of our research.

[1] Ph.D. Student, Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: laura.geambazu@gmail.com, *correspondent author
[2] Lect., Material Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: ciocoiurobert@gmail.com
[3] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: florin.miculescu@gmail.com
[4] Prof., Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: ioana.apostolescu@upb.ro

High entropy alloys benefit from specific properties, as high entropy effect, sluggish diffusion, cocktail effect and lattice distortion effect, this resulting in vast usage possibilities in different environments.

In previous work, we have studied the $Co_xCrFeMoNi$ high entropy alloy [1] produced by liquid phase, in a vacuum arc remelting furnace, where the obtained bulk material was tested in an active geothermal area for a 30-days period. Tests were conducted in Reykjanesbær Power Plant, Iceland, where the temperatures reach 200°C and pressure of 1.65 MPa. The results of this study were promising and lead to the current work.

2. Materials and Methods

In order to produce and equimolar $Co_xCrFeMoNi$ high entropy alloy by solid state processing, raw, pure, metallic powders of Co, Cr, Mo, Ni, and Fe were used. All metallic powder manipulation during the experiments was performed using a glove box, in Argon atmosphere and by using an oxygen monitor, this way avoiding contamination and excessive oxidation effects. For the entire process, the oxygen level in the glove box was at 3%.

The solid state processing was performed using a Planetary Ball Mill (Pulverisette 6, Frich®). Contamination was avoided by using stainless steel balls and vial and, by milling the powder in Argon atmosphere, the oxidation was reduced. Before the alloying process, the powders were homogenized, for 10 minutes, at a low speed.

Producing an alloy in solid state, represents an economical alternative to the liquid state processing, where coating the in work components and other surfaces do not require as much material. Other advantages are represented by the available mobility, where surfaces can be repaired or recoated in need.

After the homogenized powder was obtained, N-Heptane as PCA was added to the mixture, to improve the alloying process, the BPR used was 10:1 and the speed of 350 rpm. The mixture was milled for 30 h.

Samples were collected from the homogenized mixture but also during the process at specific periods of time and microscopically analyzed establishing the alloying degree obtained.

Samples were investigated using a Field Emission Scanning Electron Microscope (FE-SEM) for the microstructural analysis and X-Ray Energy Dispersive Spectroscopy (XEDS) equipment for the chemical composition analysis. A PANalytical X-pert Pro system was used to obtain the XRD pattern for the high entropy alloy produced in solid state.

As part of the classical metallurgy powder characterization, the $Co_xCrFeMoNi$ high entropy alloy, was dry sieved by using a Vibratory Sieve Shaker (Analysette 3 Spartan Frich®), sieves with mesh widths from 20 μm to

160 μm. Other powder characterization tests were performed by using a classic Carney funnel.

Taking in consideration that the final step is represented by coating the in work components with the high entropy alloy mentioned, the final powder will be pressed and sintered, in order to obtain a final bulk material that can be further processed. The sintering is performed in a classing metallurgy furnace and the parameters are established in accordance with the used high entropy alloy, after tests and trials. The bulk material needs to hold its shape and have a good mechanical resistance, so that electrodes can be machined and used for the coating process.

The deposition of $Co_xCrFeMoNi$ high entropy alloy, produced by electro spark deposition technique was performed by using SparkDepo® Model 300 equipment, with miniature applicator, under Argon atmosphere.

3. Results and Discussions

As mentioned, the mixture of Co, Cr, Fe, Mo and Ni, were milled for 30 h in the planetary ball mill, in order to obtain the desired high entropy alloy. By macroscopically analyzing the homogenized sample (fig. 1) and the final alloyed mixture (fig 2.) was observed that a good alloying degree was obtained and good homogenization in all its mass.

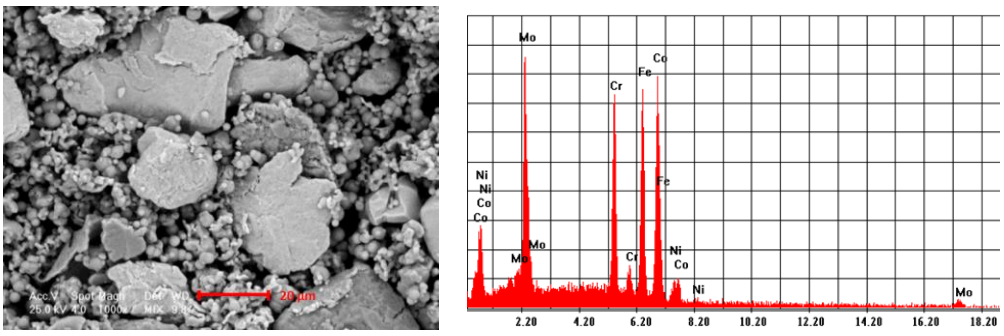

Fig. 1. SEM and EDS microscopic analyses of the homogenised mixture before MA

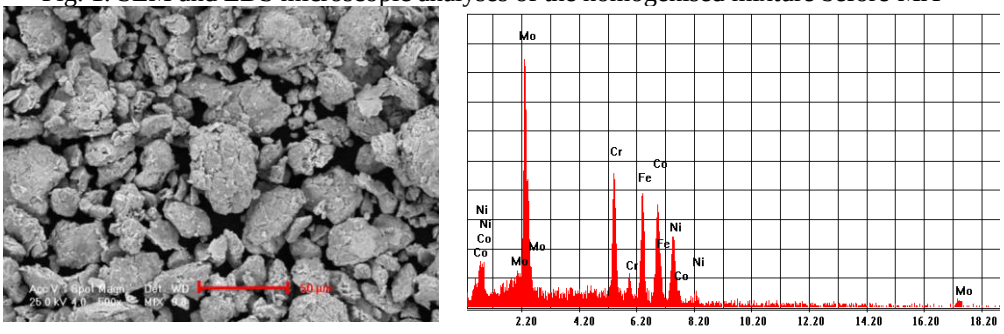

Fig. 2. SEM and EDS microscopic analyses of $Co_xCrFeMoNi$ HEA produced by MA technique

In the EDS microstructure analyses we can confirm the composition and it can be observed that there are no signs of contamination after the mechanical alloying process. The obtained desired results concluded into further processing.

After the alloying process, the powder was characterized by sieving and the results are reported in the fallowing graphic.

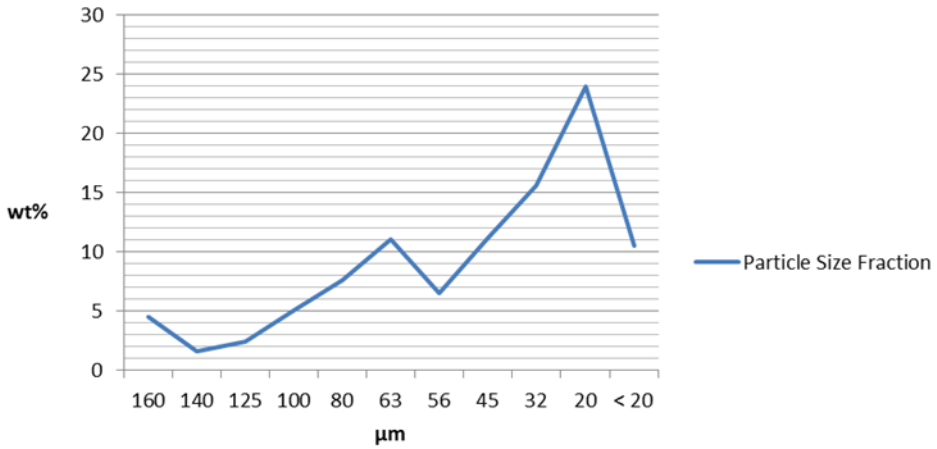

Fig. 3. Particle size fraction of $Co_xCrFeMoNi$ high entropy alloy after solid state processing

Due to the milling time, it can be observed that a high percentage of the obtained powder particle size is in the range of < 20 µm – 56 µm. Assessing particle size distributions, leads to different types of depositions (ex. powder spraying deposition in different media).

The powder characterization, performed with classic Carney funnel, provides data regarding the packing density flow and tap angle. For these experiments both raw individual metallic powders and the final alloy were tested and for each, 25g of material was used.

By characterizing the raw materials, we can determine how the milling time impacted the mixture, where the different densities of Co, Cr, Fe, Mo and Ni might affect the final results. Raw materials powder characterizations are presented in the following table.

Table 1

Metallic powder characterization of raw Co, Cr, Fe, Mo, Ni

	Free Flow Density (g/cm^3)	Tap Density (g/cm^3)	Packing Density (%)	Flow Rate (g/s)	Tap Angle (degree)
Co	2.08	2.6	80	0.57	34.21
Cr	2.45	3.2	76.6	1.2	31.79
Fe	3.12	4.05	77	0.85	9.64
Mo	4.16	4.63	89.8	9.61	21.8
Ni	4.54	5.1	89	12.19	17.74

The obtained data reveals the differences in terms of packing density and tap angle values.

The experimental results for the $Co_xCrFeMoNi$ high entropy alloy are presented in the following table.

Table 2

$Co_xCrFeMoNi$ high entropy alloy powder obtained by solid state processing characterisation

	Free Flow Density (g/cm^3)	Tap Density (g/cm^3)	Packing Density (%)	Flow Rate (g/s)	Tap Angle (degree)
$Co_xCrFeMoNi$	3,57	4.41	81	4.33	19.79

The packing density or the ratio of free flow density and tap density, determines if the powder can be further pressed or sintered. The value of 81%, indicates the possibility of further experimentation. The value is influenced by the particle size obtained after milling.

Free fall value of 19.79 degree indicates a good flow of the powder, where other types of depositions can be used. The High Velocity Oxygen Fuel deposition, requires a good flow of the powder, otherwise the installation can become clogged or damaged.

The flow was also determined by the tap angle, where the maximum value of a good flow is to be less than 35 degree, in our case the value being 14.27, confirming the results.

Pressing the samples after the powder characterization implied tests and trials, due to the fact that the novelty of the researched subject implies low literature data.

For pressing the samples, demolding wax was used for every trial. The parameters were varied in terms of particle size, material quantity, compression force or binding material as presented in table 3.

Table 3

Parameters used in order to obtain a bulk material that can be further processed

Sample identification number	Particle size (μm)	Quantity (g)	Bonding Agent	Compression Force (tf)
Sample 1	< 20	47	N-Heptane	25
Sample 2	< 20	30	N-Heptane	25
Sample 3	< 20	25	Zn Stearate	25
Sample 4	> 140	25	Zn Stearate	25

Tests revealed that the required compression pressure in order to obtain samples that will hold shape was of 25 tf, with 2% Zn stearate used as a binding element. Results are presented in Fig. 4.

By comparing the compression curves of the 4 samples, it can be observed that for sample 4, the compression evolved linear, with no disruptions and at a macroscopic analyze (Fig. 5) and can be further sintered.

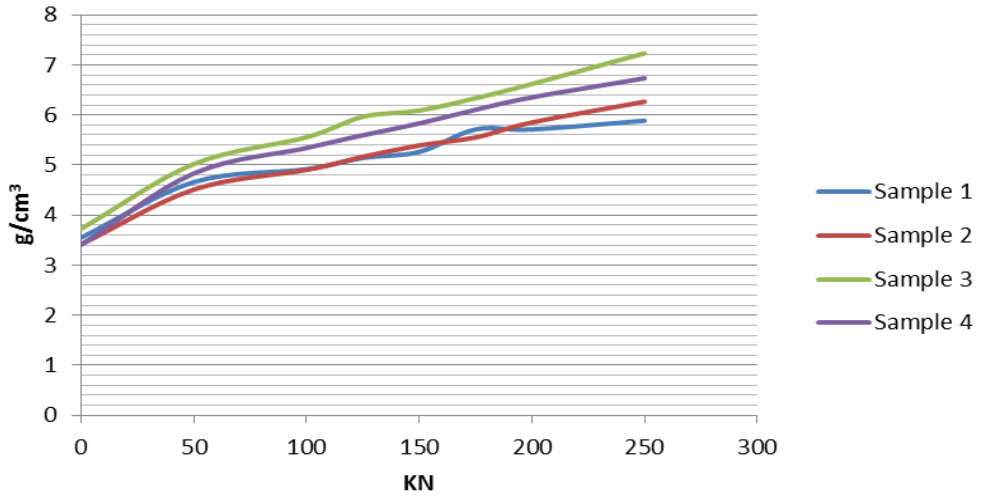

Fig. 4. Compression curve for 4 tested batches in different conditions

Fig. 5. Sample of $Co_xCrFeMoNi$ high entropy alloy after compression testing

In order to consolidate the sample, a thermal treatment was applied. The treatment is meant to increase the stability, hardness and mechanical resistance, which are necessary properties for the sample to be further processed. For sintering the sample, the parameters were selected, based on the elements present in the mixture. The protective Argon atmosphere was present in this process, so oxidation can be minimized.

Table 4

Thermal treatment parameters for the sample consolidation

Thermal treatment temperature	1100°C
Temperature increase rate	10°C/min
Temperature maintaining	1 h
Atmosphere	Argon
Cooling	with the furnace

After the sintering process, the sample was consolidated (Fig. 6) and further processed into electrodes. For producing the electrodes from the bulk material, the sample was cut and machined.

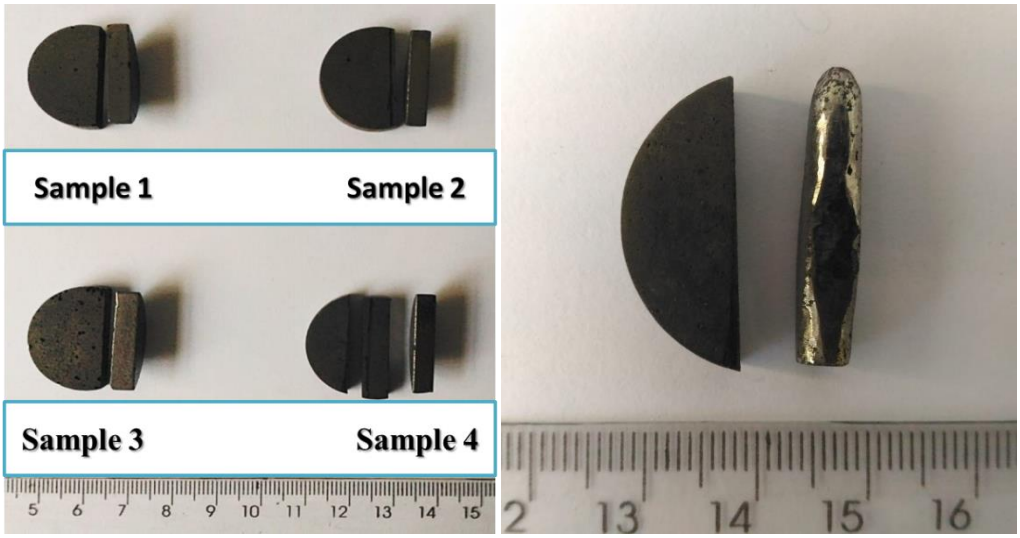

Fig. 6. The process of obtaining electrodes from bulk material for the electro spark deposition technique

In order to obtain a better resistance for the electrode during the deposition, a new and improved shape was designed. The end section, or the section that will be fixed in the applicator, will have a hexagonal shape, due to the clamping type of the applicator. The middle section of the electrode will have a high breaking predisposition, so the solution was to have a square section. The tip of the electrode has a cone shape, in order to have a smooth material deposition process. The final electrode was mechanically cleaned and degreased, to remove all impurities. The deposition parameters selected for this process are presented in table 5.

Table 5

Deposition parameters for the electro spark deposition process

Deposition Material	Substrate	Capacitance	Voltage	Frequency	Atmosphere
HEA $Co_xCrFeMoNi$	Stainless Steel	20μF	100 V	200Hz	Argon (3 l/min)

The coating was obtained by depositing successive coatings of the high entropy alloy, in order to obtain a continuous deposition, with the miniature applicator under Argon atmosphere. The Argon atmosphere is present for the entire process; therefore, the level of oxidation in the coating will be reduced to a minimum value.

In Fig. 7, the deposition process is presented.

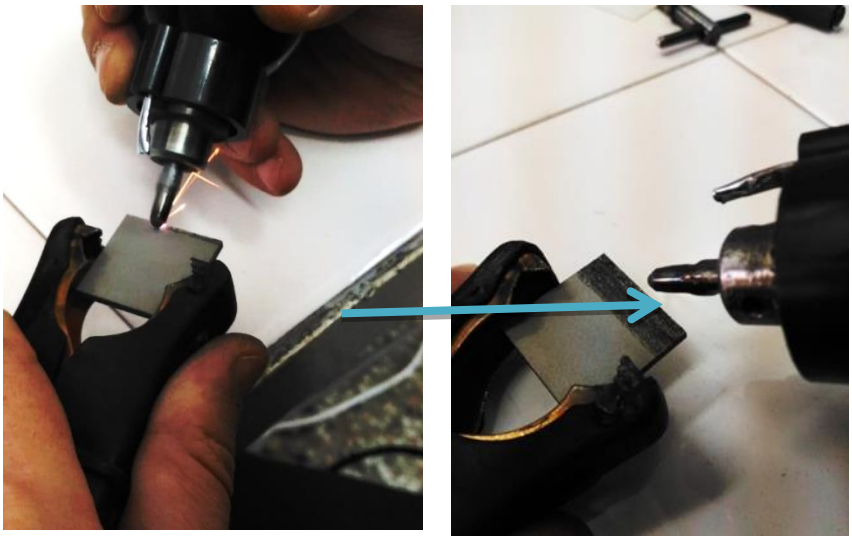

Fig. 7. Coating process performed with electro spark deposition technique

In Fig. 8 the stainless steel sample coated with $Co_xCrFeMoNi$ high entropy alloy by electro spark deposition technique is presented. From the macroscopically analysis, the coating is continuous and does not present any defects.

Fig. 8. Stainless steel sample, coated with $Co_xCrFeMoNi$ high entropy alloy

After the final coated sample was obtained, the next step was to analyze the layer in a cross section. The sample was cut, embedded in resin and metallurgical prepared. The optical analysis of the sample is presented in Fig. 9.

From the optical microstructure analyze can be observed that the coating was obtained. The layer does not present crack or adhesion failure. Pores are present, but do not affect the integrity of the deposited layer. Pores might be present due to the metallurgical preparing technique of the sample. Further analyses will be done regarding this subject.

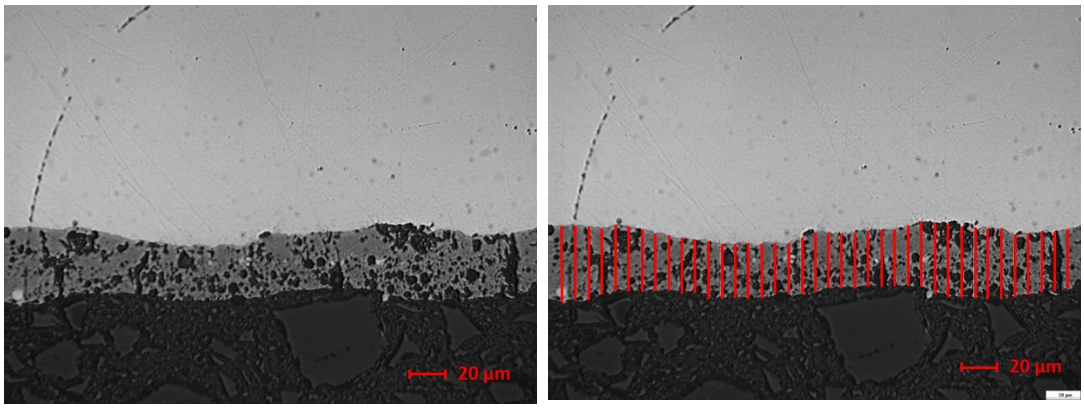

Fig. 9. Optical microstructural analyses of $Co_xCrFeMoNi$ high entropy alloy coating

In the presented figures, the coating thickness was measured. The results for the selected area show that the maximum thickness achieved is of 44.53 µm, the minimum thickness achieved is of 29.81 µm, and the mean of 35.7 µm thickness of the coating.

5. Conclusions

$Co_xCrFeMoNi$ high entropy alloy was produced by solid-state processing technique. Powder characterization was performed in terms of microscopically analyses, assessing the powder and obtaining the particle size distribution and other classic methods of characterization.

The result revealed a good alloying degree and a homogenized powder, where the particle size was predominant in the < 20 µm – 56 µm range due to increased milling time. The high entropy alloys have promising results this concluding into further processing, where the final goal of producing a resistant electrode was achieved.

A sample of stainless steel was coated with $Co_xCrFeMoNi$ high entropy alloy material by electro spark deposition method and the results are presented. The coating does not present cracks or fissures and appears to have a very good adhesion. Tests for adhesion resistance will be performed on the coated samples.

Future work will be focused on testing the obtained coating in geothermal environment with the objective of creating a corrosive-erosive resistant barrier against the aggressively of the geothermal environment.

Acknowledgements

The work has been funded by the Operational Programme Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705. This project has received funding from the

European Union's Horizon 2020 research and innovation programme under Grant agreement 764086.

REFERENCES

[1] *S.N .Karlsdottir, L.E. Geambazu, I. Csaki., A.I. Thorhallsson, R. Stefanoiu, F. Magnus, C. Cotrut*, Phase evolution and microstructure analysis of CoCrFeNiMo high-entropy alloy for electro-spark-deposited coatings for geothermal environment, in Coatings, vol. 9, no. 6, June 2019, an 406

[2] *I. Csáki, I., S.N. Karlsdottir, R. Stefanoiu, L.E. Geambazu, F. Miculescu, A.I. Thorlaksson, A.V. Motoiu*, Mechanically alloyed CoCrFeNiMo high entropy alloy behavior in geothermal steam, in NACE - International Corrosion Conference Series, vol 2019, March 2019, an. 13239,

[3] *S.S. Nene, M. Frank, K. Liu, S. Sinha, R.S. Mishra, B.A. McWilliams, K.C. Cho*, Corrosion-resistant high entropy alloy with high strength and ductility, in Scripta Materialia, vol. 166, June 2019, pp. 168-172

[4] *R.F. Zhao, B. Ren, B. Cai, Z.X. Liu, G.P. Zhang, J.J. Zhang*, Corrosion behavior of $Co_xCrCuFeMnNi$ high-entropy alloys prepared by hot pressing sintered in 3.5% NaCl solution, in Results in Physics, vol. 15, December 2019, an. 102667

[5] *S.Shuang, Z.Y.Ding, D.Chung, S.Q.Shi, Y.Yang*, Corrosion resistant nanostructured eutectic high entropy alloy, in Corrosion Science, vol. 164, March 2020, an. 108315

[6] *S.N. Karlsdottir, I. Csaki, I.V. Antoniac, C.A. Manea, R. Stefanoiu, F. Magnus, F. Miculescu*, Corrosion behavior of AlCrFeNiMn high entropy alloy in a geothermal environment, in Geothermics, vol. 81, September 2019, pp. 32-38

[7] *M.A. Hemphill, T. Yuan, G.Y. Wang, J.W. Yeh, C.W. Tsai, A. Chuang, P.K. Liaw*, Fatigue behavior of Al 0.5 CoCrCuFeNi high entropy alloys, in Acta Mater., vol. **60**, 2012, pp. 34