UNIVERSITY POLITEHNICA OF BUCHAREST MATERIAL SCIENCE AND ENGINEERING FACULTY



STUDIES AND RESEARCH ON CORROSION RESISTANCE IN AGGRESSIVE ENVIRONMENTS OF HIGH ENTROPY ALLOYS WITH VARIABLE MOLYBDENUM CONTENT

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INTRODUCTION

"The geothermal energy is stored as heat under the solid layer of the earth's surface" (Directiva RES 2009/28/CE). The advantages of the geothermal energy are in general represented by the high pressure and temperatures, by this making it possible to power with electrical and thermal energy houses, institutions but also public spaces, this representing a high percentage of the consumed energy in most regions. The disadvantages are represented by the extraction method, due to the aggressive environment, where the in work equipment are highly damaged.

The main aggressive factors are represented by corrosion, erosion and abrasion, which conduct to negative effects on the in work equipment. The factors are determined by the steam and fluids chemical compositions, being mainly composed of H_2S and CH_3 and along with high pressure, temperature and abrasive particles, result in high maintenance costs, the necessity of multiple repairs or replacing the metallic parts.

Studies and research have been directed towards this encountered problem, where the main purpose was represented by the discovery of a viable solution to increase the lifespan of the equipment, by either replacing or repairing at lower costs or by developing protective layers from materials with superior resistance to aggressive environments.

J. W. Yeh, mentions in the paper "Recent Progress in High-Entropy Alloys" [1], that the principal aspects followed when obtaining alloys are represented by wear resistance, corrosion resistance, high temperature resistance, high hardness and low density but also of obtaining ecofriendly alloys that could be recycled and reused.

The materials that are already used as coatings for motors, tools, maritime domain, nuclear domain, etc. need to be improved even though they provide the requested aspects mentioned earlier [1]. By this, the high entropy alloys were studied more recently, becoming a viable solution for this type of media.

High entropy alloys as reported present superior properties and unique, being characterized by the 4 core specific effects which are the high entropy, severe lattice distortion, cocktail effect and sluggish diffusion.[1]

The main goal of this PhD Thesis, is to obtain a high entropy alloy, with superior properties, good corrosion resistance but also a good resistance to other aggressive factors, which can represent a solution of the in work equipment from the geothermal energy. The goal is to obtain a material where the costs will be lower than the existent procedures.

The first chapter of this PhD Thesis was dedicated to the literature review of the geothermal data available locally and globally, where this type of renewable energy is in use.

The studies related to this topic, started during the Master's Degree where in the paper "Studies and research on the corrosion resistance in geothermal environment of the CoCrFeNiMo high entropy alloy", I presented promising results on the corrosion resistance of the CoCrFeNiMo high entropy alloy processed by vacuum arc remelting, which was tested in geothermal steam. This lead to more in depth research regarding the topic, where the experimentation was also focused on reducing the costs of the final product.

First experimentations consisted of obtaining electrodes from the produced alloy by mechanical processing and layers deposition by electro spark deposition technique. The analyzed coating revealed good results.

The high production costs for the CoCrFeNiMo high entropy alloy produced by vacuum arc remelting process lead to other processing methods, which will not affect the performances.

For this Thesis, I studied the option of processing the mixture by mechanical alloying in a mono planetary ball mill. After the high entropy alloy was obtained, it was metallurgical

characterized in order to determine the alloying degree and the homogeneity, but also the mechanical processing possibility.

In order for the electrodes to be produces, the powder material was pressed and sintered, followed by cutting and mechanical processing of the bulk material into the final electrodes.

The coating was obtained by electro spark deposition process from the studied high entropy alloy, deposited on stainless steel under Argon atmosphere. The coatings were further analyzed by mechanical and chemical testing and the results are presented.

I decided to perform a adhesion testing for the obtained coating, for which a testing device was manufactures, from as few resources as possible, which is adaptable to a certain extent for samples with variable dimensions. The results obtained were relevant and promising, because the deposited layer did not undergo changes or exfoliations.

From an economic point of view, I made calculations for the production cost of coatings obtained by the electric spark deposition technique (Electro Spark Deposition) for which I had as reference costs of a geothermal turbine blade, but also the costs of maintenance for the Hellisheiði geothermal power plant in Iceland.



Reykjavik, Islanda, 2018

PART I: THEORETICAL STUDY ON ALLOYS WITH COMPLEX COMPOSITION FOR GEOTHERMAL ENVIRONMENT USEAGE

1.1. Current State of Geothermal Energy and Materials Used in the Industry

The geothermal energy is an important renewable energy resource, which presents a high interest due to reliability, durability, low costs and energy efficiency [2].

This resource is based on the natural underground heat and can be extracted]n underground water reservoirs and rocks by conduction and convection [3].

From the data publicated by the Global Geothermal Alliance (GGA), can be observed a continous growth of the energy production capacity and the chart is presented in figure 1.1.



Fig. 1.1. Increasing the thermal capacity installed in recent years globally according to data published by IRENA

1.2. Geothermic Energetic Potential of Romania

The hidro-geothermal resources temperatures at the national level is in general between 25° C - 115 °C, and the exploitation of geothermal deposits began in 1962. The deepest drillings were located in the capital area and reach depths of 3300 m

The following table presents current data on the use of geothermal energy in Romania [4,5].

During the last 25 years, the experimental exploitation of the deposits has been tried, by drilling about 100 wells, and the use of the extracted geothermal energy is in the following proportions [6]:

Studies and Research on Corrosion Resistance in Aggressive Environments of High Entropy Alloys with Variable Molybdenum Content

Table 1.1. Geothermal applications at national level [4]						
Location	Temperature	Wells	Thermal	Usage		
			Energy			
Oradea	75 °C − 105	12 - 11	cca.	15% of the thermal energy needs of the		
	°C	wells	100.000	population of Oradea Municipality. The		
			Gcal/year	main beneficiaries are universities,		
			-	hospital, hotels, Olympic pool, etc.		
Beiuş	70 °C – 84 °C	2 wells	25.000	The only city in the country, which		
			Gcal/year	relies almost entirely on thermal energy		
			-	from geothermal systems, to heat		
				homes		
Livada	90°C	well with	8.585	The first greenhouse in Romania with		
		debit of 12 -	Gcal/year	tomatoes in a bio-ecological system,		
		201/s		with a production of 800t / year		
Perimetrul	80 °C	6 sonde de	90.000	Space heating, balneology,		
Săcuieni		producție	Gcal/year	greenhouses, livestock farms and		
		_		aquaculture,		
Perimetrul	92 °C	1 sondă	16000	Green houses		
Ciumeghiu			Gcal/year			
Perimetrul	85 °C	1 sondă	10.400	Space heating		
Cighid			Gcal/year			

Different forms of geothermal corrosion are generally caused by the direct contact between the steam and fluids with the geothermal pipes, in work equipment and parts. Studies have multiple reports from different geothermal power plants as a base. [7-11].

Uniform corrosion can be described as a chemical or electrochemical reaction that can happen on an entire exposed surface, which affects the thickness of the used materials. The effects are presented in the next figure [12, 13]



Fig. 1.2. Uniform corrosion (left) observed on the roof of a geothermal well. Deep scratches (right) on the main valve wall indicate the erosion-corrosion phenomenon. The proof in the image is the property of Chris Morris (Energy Ltd)

Current utilized method for improving the working time of the in work equipment's that are attacked by the uniform corrosion, is through applying different coatings or by adding multiple layers of the carbon steel which is currently used. Even if measurements are taken, the damage can still progress in a constant or accelerated rhythm.



Fig. 1.3. Cross section of the condenser wall of a geothermal power plant, made of carbon steel. The wall was perforated due to corrosion and was patched 3 times with steel plates. The picture on the right shows the 4 layers seen from the side. Property of Chris Morris (Energy Ltd).

The corrosion-erosion effect can be observed when there is a relative movement between the corrosive fluids and the immersed metallic materials in those fluids, resulting in an accelerated corrosion.



Fig. 1.4. The erosion-corrosion phenomenon occurred at the bending area of a mild steel pipe, the pipe that transported the water collected from the turbine housing. The proof in the image is the property of Chris Morris (Energy Ltd)

Fig. 1.5. Damage caused by erosion-corrosion on some samples, caused by the action of high-speed acidic geothermal fluid. The proof in the image is the property of Chris Morris (Energy Ltd) Fig. 1.6. Erosion caused by water droplets on the blade of a geothermal turbine, made of 410 stainless steel. The proof in the image is the property of Chris Morris (Energy Ltd)

Metallic and non-metallic materials can be used as replacing materials for some of the cases where some in work parts have direct contact with the corrosive environment. The materials can be used as exchange parts or as coatings. By coating the surfaces, costs will be reduced and the protection layer will have a high efficiency [14, 15].

The geothermal steam is mainly composed of H_2S si CO_2 and by combining it with abrasive particles, high pressure and high temperatures, result in a very fast wear of the components that work in that media.

Due to the high costs of maintenance and the necessary time for transportation and fixing of the parts, the efficiency is affected. Researches are focused on finding a suitable material for this type of environment, with superior properties, but also that will reduce the general costs.

1.3. Theoretical considerations on high entropy alloys

High entropy alloys or multicomponent alloys (HEA) can be defined as alloys composed from 5 or more distinct metallic materials, obtained elaborated by different metallurgic techniques, with distinct effects and remarkable properties, where each

composing element brings it's attributes to the final alloy. The conventional alloys are mainly composed by 1 or 2 main materials, selected accordingly to their properties, where other different materials are added in order to improve the final properties.

These relatively new alloys from the metallurgical domain are studied more and more in recent works. First researches and theories related to obtaining alloys with equimolar compositions, by mixing different metallic materials and avoiding of the "main material" concept, was firstly discussed more than a decade ago. The "high entropy alloy" concept was firstly suggested by Yeh.et. al. [16, 17], where it was suggested the concept of high configurational entropy of random mixing of elements from these alloys [16-22].

The literature [17, 18] shows the high entropy alloy as an alloy that can be modeled in an ideal solution, the configurational entropy of the mixture per mole being expressed by equation 1.

$$\Delta S_{mix} = -R \sum_{i=1}^{n} c_i \ln c_i \tag{1}$$

High entropy can be obtained for the multicomponent alloys case, by increasing to mixing entropy, this being directly proportional with $\ln n$, where solid solutions formation possibility increases according to equation 1.

High entropy alloys, as Yeh et.al. first proposed them as [23,24], were composed from a series of elements in equimolar proportions or almost equimolar, based on the concept of high configurational entropy, which favors the formation of solid solutions with one phase, two phases or with several phases.

Recently, for the high entropy alloys from the CrCoNi system, Gludonatz et.al. [25] reported superior properties as such as the high breaking strength of Contor alloy at both cryogenic and room temperatures, but high radiation resistance has also been reported compared to pure elements [26].

High entropy alloys can be analyzed following their specific effects, which contribute to the large number of researches and studies on these materials, these effects being high entropy, severe lattice distortion, the "cocktail" effect and the sluggish diffusion effect [23].

PART II – THERMODYNAMIC STUDY ON THE CoCrFeNiMo HIGH ENTROPY ALLOY SYSTEM WITH A VARIABLE MOLIBDENUM CONTENT

2.1. Thermodynamic calculations for the high entropy alloys

High entropy alloys have their unique characteristics due to the multicomponent solid solution formation, according to literature [27-32].

According to Zhang et.al [32] in order to be able to characterize the collective behavior of the constituent elements from the high entropy alloys, 3 parameters were used, them being namely the enthalpy of mixture (ΔH_{mix}), the entropy of the mixture (ΔS_{mix}) and the difference in atomic size (δ), and these are defined by the equations 2, 3 and 4.

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{N} \Omega_{ij} c_i c_j$$
⁽²⁾

where $\Omega_{ij} = 4 \Delta_{mix}^{AB}$, iar Δ_{mix}^{AB} 78 / 5000 is the enthalpy of mixing pairs of liquid AB alloys.

The range of pairs with chemical interaction forces will tend to increase as the number of constituents increases, resulting in strong chemical interactions to reduce enthalpy.

$$\Delta S_{\rm mix} = -R \sum_{i=1}^{n} c_i \cdot \ln c_i \tag{3}$$

where n is the number of elements, R is the gas constant and c_i is the concentration of the element i.

$$\delta = 100 \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{4}$$

Where n is the elements number, r_i is the atomic radius of the element c_i is the concentration of the element i.

$$\bar{\mathbf{r}} = \sum_{i=1}^{n} R_i \cdot c_i \tag{5}$$

In the paper published by Sheng G. et al. [27] electronegativity χ was taken into account, starting from the Pauling equation, being defined as

$$\chi = \sum_{i=1}^{n} E_i \cdot c_i \tag{6}$$

The Valence Electron Concentration (VEC) parameter, determines the intermetallic compounds phase stability. According to G. Sheng. et.al [27], when the calculated VEC value is under 6, there will be more FCC phases and if the value is over 8 there will be more BCC phases. When VEC value is between 6 and 8, according to the. theory there will be found a mixture between FCC and BCC phases

$$\text{VEC} = \sum_{i=1}^{n} \text{VEC}_{i} \cdot c_{i} \tag{7}$$

Where n is the number of elements, VEC_i is the VEC of the element i and c_i is its concentration. The influence of the amount of Molybdenum on the melting temperature on the final alloy was determined by equation 8.

$$T_{\rm m} = \sum_{i=1}^{n} c_i \cdot T_i \tag{8}$$

Where T_i is the melting temperature of the element i and the derived parameter Ω is calculated with equation 9.

$$\Omega = \frac{T_m \cdot \Delta S_{mix}}{\Delta H_{mix} \cdot 1000} \tag{9}$$

This thermodynamic study has been realized with the main purpose of selecting the most appropriate composition from a thermodynamically point of view from the CoCrFeNiMo system, that can be further used in the geothermal environment.

The alloys for this type of environment have to must have high corrosion resistance and another condition is that they can be easily processed after compaction, in order to obtain electrodes for depositing layers. The properties of the constituent elements of the studied high entropy alloys are presented in table 2.1., In which the atomic number, atomic radius, elementary electronegativity, VEC and melting temperature were taken into account.

I ubica	Tuble 2.1. Constituent high entropy andy elements properties						
Element	Atomic No.	R (Å)	Electronegativity	VEC	T _{melting}		
Co	27	1.670	1.88	9	1495		
Cr	24	1.850	1.66	6	1857		
Fe	26	1.720	1.83	8	1535		
Ni	28	1.620	1.91	10	1453		
Mo	42	2.010	2.16	6	2617		

Table.2.1. Constituent high entropy alloy elements properties

For this paper, the thermodynamic calculations were made for the CoCrFeNiMo high entropy alloys system with variable concentration of Molybdenum in order to observe it's influence on the final alloy. The element concentration for each alloy is presented in the following table.

Constituent	Co	Cr	Fe	Ni	Мо		
elements	[% at.]						
CoCrFeNiMo _{0,5}	0,225	0,225	0,225	0,225	0,1		
CoCrFeNiMo0,85	0,2075	0,2075	0,2075	0,2075	0,17		
CoCrFeNiMo	0,2	0,2	0,2	0,2	0,2		
CoCrFeNiMo _{1,5}	0,175	0,175	0,175	0,175	0,3		
CoCrFeNiMo ₂	0,15	0,15	0,15	0,15	0,4		

Table.2.2. Elements concentration for the CoCrFeNiMo high entropy alloys system

The thermodynamic calculations for the CoCrFeNiMo high entropy alloys system alloys comparative results are presented in the following table.

	anoys with variable concentration of Worybacham						
	CoCrFeNiMo _{0,5}	CoCrFeNiMo _{0,85}	CoCrFeNiMo	CoCrFeNiMo _{1,5}	CoCrFeNiMo ₂		
VEC	8.0250	7.8675	7.8000	7.5750	7.3500		
Ē	1.7445	1.7652	1.7740	1.8035	1.8330		
δ	6.8847	7.6761	7.9287	8.4824	8.6743		
χ	1.8540	1.8778	1.8880	1.9220	1.9560		
ΔS_{mix}	13.0695	13.3501	13.3744	13.1404	12.5048		
ΔH_{mix}	-4.9523	-4.7283	-4.6240	-4.2403	-3.8010		
T _m	1961.20	2033.44	2064.40	2167.60	2270.80		
Ω	-5.1758	-5.7413	-5.9711	-6.7173	-7.4706		

Table 2.3. The thermodynamic calculations for the CoCrFeNiMo high entropy alloys system alloys with variable concentration of Molybdenum

According to the obtained results after the VEC calculations I decided to continue my experiments with CoCrFeNiMo which has the value of 7,8 and CoCrFeNiMo_{0,85} which has the value of 7,86. The values are close to each other and they result in a mixture of FCC and BCC phases for both cases [27]. The advantage of having both of the phases is that the material will have a good ductility but also a good resistance.

PART III - OWN STUDIES AND EXPERIMENTAL RESEARCH

3.1. Processing of CoCrFeNiMo_x High Entropy Alloy 3.1.1. Processing of CoCrFeNiMo High Entropy Alloy by liquid state processing

In order to produce CoCrFeNiMo high entropy alloy, first studies were focused on the vacuum arc remelting method.

The experimental phase and testing in the geothermal environment of the CoCrFeNiMo high entropy alloy, produced by the liquid phase method, was performed during the preparation of the dissertation, entitled "Studies and research on corrosion resistance in geothermal environment of the CoCrFeNiMo high entropy alloy". The results were disseminated at the "International Scientific Conference on Advances in Mechanical Engineering" 12-14 October 2017, Debrecen, Hungary, the paper entitled "High Entropy Alloys In Geothermal Environment" [33].

Most high entropy alloys are obtained using the liquid phase method, by Bridgman induction or solidification [34], but they can also be obtained by gas phase processing or solid state processing. [34-38]. The high entropy alloy CoCrFeNiMo was obtained by vacuum spring remelting, in the ERAMET laboratory, JK 001. For these experiments were used materials with a high purity, cast state and the composition of the alloy being presented in table 3.1

	at%	М	M*at%	W%	m,[g]
Co	20	58.933	1178660	24	6
Cr	20	51.996	1039920	21	5.25
Fe	20	55.847	1116940	22	5.5
Ni	20	58.693	1173860	24	6
Mo	20	95.940	1918.8	9	2.25

Table 3.1. CoCrFeNiMo high entropy alloys composition

In order to obtain the alloy, a copper matrix was used, with disk shape chambers. The material was remelted for at least 5 times in order to obtain a very good homogeneity in all its mass. The final sample weight was of 25 g / sample.



Fig. 3.1. Microscopic analyses results of the as cast sample surface.

The samples were corrosion tested in geothermal steam for a period of 30 days. After this period, on the samples surface could be observed a thin grey film deposition. It could also be observed that selective oxidation was present which can be related to the homogeneity level of the final material.



Fig. 3.2. Samples of CoCrFeNiMo after exposing



Fig.3.3. a. Before; b. After chemical and mechanical cleaning

The samples were cleaned both chemically and mechanically according to the standard for after exposure sample cleaning ASTM G4 Conduction, and the preliminary results are very favorable after the corrosion rate results. The calculations were made for the exposure of 720 h where K= 87600 mm/year, for a density of 8,42751 g/ cm³ [33]

Table 3.2. Corrosion rate for CoCrFeNiMo high entropy alloy after 30 days of geothermal steam exposure

HEA	Sample No	A surface[cm2]	W weight loss [g]	Corrosion Rate (K*W)/(A*T*D) [mm/year]
	1	16.15130482	0.00037	0.000330725
CoCrFeNiMo	2	16.43522469	0.00044	0.0003865
	3	13.68792547	0.00031	0.000326961

The results presented a weight loss of approx. 0.00233%, this value being very good for corrosion testing in that type of media. The microscopic analyses results are present in the following figures.



Fig. 3.4. SEM analyses results of the as cast sample surface after exposure

For this case, the results present the surface oxidation, but the structure was not affected by the geothermal steam, this leading to other types materials processing methods in order to reduce the costs of the final material.

6.2. Processing of CoCrFeNiMo_{0.85} High Entropy Alloy by Mechanical Alloying

Due to the results obtained in the first experimentation, the next step was to identify a more economical efficient method of processing of the alloy, where the final result will be a material with very good corrosion resistance.

In order to obtain the alloy with a higher degree of alloying an homogeneity, mechanical alloying was taken into consideration, this method also having reduced production costs.

The metallic powders of Cobalt, Chromium, Nickel, Molybdenum and Iron with a purity as high as 99,9%, and particle dimension of approx. $63 \mu m$.

The particle dimensions are close, in order to have a higher efficiency of the time required for mechanical alloying, but also a high degree of alloying.

I decided to add a control agent in the composition, in order to perform a wet milling, having the advantage of obtaining a high degree of alloying, but also to avoid very high temperatures inside the vial, which induce welding of the material of the vial walls. The control agent or PCA used is N-Heptane. It acts as a lubricant for both balls and vial, as well as for the metallic powders, evaporating during grinding, but also during the following processes where the temperature is high, the boiling temperature of N-Heptan being 98.42 $^\circ$ C .

During the process, at regular intervals, samples were taken and analyzed by electron microscopy - SEM, but also by EDS analysis. to decide the time required to obtain the high entropy alloy CoCrFeNiMo_{0.85}.

Figure 3.5 shows the microscopic analysis of the homogenized powder in the ball planetary mill for 10 minutes. ESD analysis confirms the initial composition, and the peaks indicate the individual presence of pure component materials. It can also be observed the absence of oxygen, but also other types of impurities.



Fig. 3.5. SEM and ESD analyses results of the homogenized metallic powder of CoCrFeNiMo_{0,85}

After 150 min of milling, a sample was taken and analyzed and the results are presented in the following picture. It can be observer the beginning of the mechanical alloying by particle agglomeration and particle dimensions reductions. The mixture composition was confirmed where no oxygen is present in the composition, but also no other impurities.

Studies and Research on Corrosion Resistance in Aggressive Environments of High Entropy Alloys with Variable Molybdenum Content



Fig. 3.6. SEM and ESD analyses results of the metallic powder of CoCrFeNiMo_{0,85} alloyed for 150 min

In figure 3.7., The dimensional uniformity of the particles and the beginning of the mechanical alloying can be observed, after an effective milling time of 225 minutes. Furthermore, there are no impurities of the material with oxygen.



Fig. 3.7. SEM and ESD analyses results of the metallic powder of CoCrFeNiMo0,85 alloyed for 225 min

Figure 3.8 shows the analysis of the mixture after an effective milling time of 300 minutes. The analyses indicate an increase in the degree of alloying and homogenization.



min

SEM and EDS analyses of the CoCrFeNiMo_{0,85} mixture after an effective milling time of 375 minutes are shown in Figure 3.9. These indicate an almost complete degree of alloying and lack of oxygen in the mixture.



Fig. 3.9 SEM and ESD analyses results of the metallic powder of CoCrFeNiMo0,85 alloyed for 375 min

Figure 3.10 shows the results of the microscopic analysis performed after an effective milling time of 450 minutes. These indicate a high degree of alloying in a relatively short time.



Fig. 3.10. SEM and ESD analyses results of the metallic powder of CoCrFeNiMo0,85 alloyed for 450 min

ESD analysis confirms the initial composition, without traces of oxygen or other types of contamination. The metal powder is homogenized throughout the mass, and the metallic particles reduced their dimension. The initially added control agent was consumed during the process, not being present in the final composition [39, 40].

In conclusion, the high entropy alloy CoCrFeNiMo_{0,85} was obtained by the mechanical alloying process and can be processed later. The initial experiments consisted in the characterization of the constituent powders of the alloy with high entropy CoCrFeNiMo_{0,85}, and the results are presented in the following table.

Metallic material	Average particle dimension (μm)	Free flow density (g/cm3)	tap density (g/cm3)	packing density (%)	Flow rate (g/s)	slope angle (degrees)
Nickel	37	4,54	5,1	89,0	12,19	17,74
Molybdenum	44	4,16	4,63	89,8	9,61	21,8
Cobalt	74	2,08	2,6	80,0	0,57	34,21
Iron	96,5	3,12	4,05	77,0	0,85	9,64
Chrome	31,5	2,45	3,2	76,6	1,2	31,79

Table 3.3. Metallic constituent powders of the high entropy alloy

The results obtained after the metallic powder characterization obtained by mechanical alloying are presented in the following table.

Table. 3.4. CoCrFeNiMo_{0,85} high entropy alloy metallic powder characterization, obtained by mechanical alloying

Alloyed metallic powder	CoCrFeNiMo HEA
Used equipment	Carney Funnel
Flow rate	4.33 g/s
Free flow density (ρ _{lv})	$3,57 \text{ g/cm}^3$
Tap density (ρ _t)	4.41 g/cm^3
Packing density	81 %
Slope angle	19.79°

Using the Carney funnel, the flow rate was determined to be 4.43 g / s, indicating that this powder can also be used for coatings by other procedures such as High Velocity Oxygen Fuel. Figure 3.11 shows graphically the difference in powder flow rate before and after mechanical alloying.



Fig 3.11. Flow rate before and after mechanical alloying

The density of free flow obtained experimentally, has the value of $3.57 \text{ g} / \text{cm}^3$, and the density in compacted state has the value of $4.41 \text{ g} / \text{cm}^3$. The packing density represents the ratio between the free-flowing density and the compacted density obtained and has the value of 81%, a very good value for this powder. The packing density indicates the ability of the powder to be further processed by compaction and sintering.

3.2. Pressing and Sintering Process of the CoCrFeNiMo_{0,85} High Entropy Alloy

For samples M_P1-M_P4 stearic acid was added as binder, in proportion of 2%, and for sample M_P5 we did not use binder, the material being in the initial state, obtained after mechanical alloying. The homogenization of the metallic powders with the chosen binder was performed in the planetary ball mill. Stainless steel balls and vial were used, and the parameters of the homogenization process being 220 RPM, with a ratio of 5: 1 BPR, with the effective homogenization time of 15 min. The compressibility curves for the high entropy alloy CoCrFeNiMo_{0,85} are shown in figure 3.12. Following the obtained graph, the behavior of the material during pressing can be observed, the variations regarding the piston displacement being relatively small, thus not influencing the final results.



Fig.3.12. Compresibility curves for the alloyed materials

Sintering was performed under an argon atmosphere to avoid oxidation during the process. The rate of temperature rise during the sintering process was $10 \degree C / min$.

Tuble 5.5. Sintering parameters used to consolidate the samples						
	Temperature (°C)	Mentaining (min)	Cooling			
Dewaxing	550	60	-			
M_P1	800	60	in air			
M_P2	950	60	in air			
M_P3	1100	60	in air			
M_P4	1100	60	in furnace			
M_P5	1100	60	in furnace			

 Table 3.5. Sintering parameters used to consolidate the samples



Fig 3.13 Sintering curve for CoCrFeNiMo_{0,85} HEA samples

After sintering, the samples were characterized and the results are presented in the following table.

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Table 3.6. Obtained data after the sintering process								
Sample	H(mm)	Dia.(mm)	Mass (g)	Volume (cm ³)	ρ (g/cm ³)	Porosity %		
M_P1	5,02	25,3	15	2,523682	5,9436964	32,91539047		
M_P2	5,25	25,7	15,44	2,723425	5,66933166	36,01205797		
M_P3	4,95	25,82	14,41	2,591836	5,55976486	37,24870356		
M_P4	4,95	25,84	14,65	2,595853	5,64361691	36,30229226		
M_P5	5,04	26,2	14,46	2,717209	5,32163756	39,93637069		

Following the sintering heat treatment, the samples show an oxide layer on the surface. The samples were then prepared metallographically, by classical metallurgical methods. The comparative graph of the densities obtained after pressing the samples, but also after the sintering process is presented in figure 3.14, and in figure 3.15 is presented the porosity difference.





Fig.3.15. Before and after consolidating sample porosity

Figure 3.16 shows the results of the analyses for sample M_P4. This sample was sintered using the same parameters as in the case of sample M_P3, but the cooling was done in an oven in an argon atmosphere. In the sample structure a better compaction can be observed compared to the previous sample, where no cracks or pores are present. This sample was subsequently debited and there were no integrity issues. The results of the EDS analyses for the surface and for the light gray area confirm the composition, without the presence of impurities or oxides that could have appeared during the sintering process in the furnace.



Fig.3.16. SEM and ESD analyses results of M_P4 sample after sintering

3.3.1. CoCrFeNiMo_{0,85} high entropy alloy deposited by ESD technique

To obtain electrodes with dimensions specific to ESD deposition equipment, the bulk material was processed mechanically.



Fig. 3.17. a). Samples after melting b). Samples after heat dissipation treatment c). The obtained electrode

The deposition was performed by using the parameters presented in the following table:

Table 3.7. Parameters used for electro spark deposition with electrode obtained by the liquid phase method

Material de depus	Substrat	Capacitanță	Tensiunea	Frecvența	Atmosferă
HEA CoCrFeNiMo	Oţel - carbon	40µF	100 V	4	Argon (3 l/min)

The deposition is made in the atmosphere of Argon, in order not to form oxides on the surface, and the movement must be continuous, in order to obtain a uniform layer.



Fig. 3.18. Analyses results for the cross section of the obtained coatig

In order to obtain a microstructural analysis of the deposited layer, the sample was cut transversely and analyzed from a compositional and structural point of view. The results of the microscopic analyses are presented in figure 3.18. A uniform and homogeneous deposited layer can be observed on the entire surface of the substrate and a good adhesion of the deposited layer to the substrate. The results of the EDS analysis confirm the composition of the hyperentropic alloy used, but also the fact that during the deposition no oxides or other types of undesired contaminations appeared as can be seen in figure 3.18. In figure 3.18, the results of the analyses confirmed the composition of the obtained coating, which has a good adhesion to the substrate, is compact and has no pores or defects [41,42].

3.3.2. Electro Spark Deposition of CoCrFeNiMo_{0,85} HEA with electrodes obtained by mechanical alloying

The coating for this experiment was made on a stainless steel substrate, prepared by sandblasting, to increase the roughness and remove impurities and clean it with high purity alcohol. Following the selection of the final material, the sample was cut and mechanically processed, in order to obtain an electrode, which was later used for electrical deposition by sparks. The obtained electrode is shown in the following figure.



Fig. 3.19. HEA CoCrFeNiMo_{0.85} electrode obtained for ESD process

The appearance of the phenomena of shearing, friction, but also of the high temperature during the process of electrical deposition by sparks, the electrode made by mechanical processing, needs high resistance. The selection area for the electrode is represented by the middle area of the sample, thus obtaining the maximum possible length. The optimization of the deposition process consists in finalizing the final shape, for an efficient deposition and a high mechanical resistance of the electrode.

Table 3.8. ESD parameters for the electrode obtained by the solid phase method
deposited on a stainless steel substrate

Material	Substrate	Capacitance	Voltage	Frequency	Atm
HEA	Stainless	20µF	100 V	20014-	Argon (3
CoCrFeNiMo _{0,85}	Steel 316 L			20082	l/min)

The coating was made by successive depositions of thin layers, in order to obtain a uniform coating with the miniature electric applicator [39]. The deposition was performed under an argon atmosphere throughout the process, thus reducing the level of oxidation during the process.



Fig.3.20. Deposition of thin layers a) with electrode obtained by mechanical alloying b) with electrode obtained by vacuum arc melting

Figure 3.20 shows the results of surface SEM analyses, performed with two types of sensors, but also topographic images.



Fig. 3.21. SEM analyses results of the obtained coating surface

A homogeneous plateau was observed on the analyzed surface, with areas where there are incomplete zonal melts, which can be caused by the temperature during the deposition process or the rapid cooling. In figure 3.21, a uniform layer can be observed, the topography of the surface presenting a certain degree of roughness.



Fig.3.22. CoCrFeNiMo_{0.85} HEA coated stainless steel cross-sectional analysis results for (a) SEM image of the deposited surface (b) SEM cross-sectional image (c) EDS analysis results

The results of the SEM and EDS microstructural analyses are presented in Figure 3.22. Following the results obtained by optical microscopy, the layer thickness is confirmed, and the EDS analysis confirms the lack of contamination that could have been present during the deposition process [40]. The results of the analyses obtained in the cross section of the deposited sample confirm the surface porosity on the surface only, but it presents a compact, homogeneous layer with a good adhesion in the structure. An interference of the layer with the substrate could be observed from the EDS analysis. Although the layer of CoCrFeNiMo_{0.85} HEA was obtained by mechanical alloying, conventional pressing and sintering in the furnace, followed by mechanical processing of the electrode, no pores are present in the area of the interface between the layer and the substrate.

3.4. Mechanical and chemical testing of the deposited layer of CoCrFeNiMo0,85 HEA deposited by the ESD technique

3.4.1. The results of the roughness measurements of the deposited layer

Following the ESD deposition, I performed an analysis of the roughness of the coated surface to determine the quality of the deposited layer by comparing the level differences in different areas of the sample. The average roughness for the analyzed areas is between 4.62 μ m and 6.05 μ m. Although spark deposition is a manual process, the differences in surface topography are not noticeable. Another major influence is given by the shape of the electrode, the type of applicator, but also the way of using the equipment. From a qualitative point of view, it was obtained a homogeneous, uniform layer, without major surface defects.

3.4.2. Results of Vickers hardness measurements of the coated sample

Vickers hardness testing for the 316 L stainless steel substrate, the sample pressed and sintered in the CoCrFeNiMo_{0,85} furnace and of the layer deposited from the same alloy by ESD deposition technique, was performed with echipamentul Shimadzu Vickers hardness device (Shimadzu, Columbia, USA) with a load of 0.98 N. For each test tested, 10 measurements were made at different points, and the average value obtained was calculated. After calculating the average hardness measurements, we could observe a highest value was obtained for the CoCrFeNiMo_{0,85} HEA in sintered form, compared to the stainless steel substrate, even if the results of the characterization of the sintered sample show a slight porosity in the structure. The average value of the measured hardness of the deposited layer is 185.5 HV. This value could have been influenced by both the thickness of the deposited layer and the roughness of the surface. It also indicates a lower possibility of the formation of surface microcracks, specific to electrical deposition by sparks.

3.4.3. Adhesion Testing by Tearing Method (Pull-off Testing)

In order to perform the adhesion test by tearing method, I used as adhesive, twocomponent commercial type epoxy resin, with an adhesive strength of about 21 MPa. The results obtained from the adhesion test are correlated with the load graphs generated by the equipment used and are presented in figure 3.23.



Fig. 3.23. Grafice de încărcare din timpul testării adeziunii

From the test graphs presented in figure 3.23 can be observed the failure moment of the epoxy resin, this being the moment when the highest pulling force is applied during the test. According to the results obtained, there are no cohesive or adhesive tears during the process for both types of samples, indicating a better adhesion of the layer to the substrate compared to the adhesion of the resin to the substrate. The maximum yield strength of the adhesive was 0.67 MPa for the electrode obtained from the molten material and 0.33 MPa for the electrode obtained by mechanical alloying and compaction.

3.4.4. Corrosion Testing for CoCrFeNiMo0.85 HEA oobtained by ESD technique

The corrosion resistance of the CoCrFeNiMo_{0.85} coating obtained by the electric spark deposition technique was determined by the linear polarization technique with the Potentiostat / Galvanostat equipment. The tests were performed in an electrochemical cell, equipped with a saturated calomel electrode (SCE) being the reference electrode, the recording electrode being a platinum electrode, and the tested sample represented the working electrode. The working parameters consisted in the saline medium with a concentration of 3.5% NaCl at a temperature of 25 ± 0.5 ° C for a period of 6 hours [39].



Fig.3.24. Evolution of open circuit potential (a) and Tafel graphs (b) for coating CoCrFeNiMo_{0.85} high entropy alloy obtained by the EDS deposition technique

The parameters of the electrochemical test are presented in Table 3.9 and were determined to characterize the corrosion resistance of the coated sample according to ASTM G5-94 (2011) [43], where E_{oc} represents the open circuit potential, E_{corr} is the corrosion potential and the current density. corrosion is I_{corr} [39]. The polarization resistance test was performed according to the Stern-Geary equation [44], and equation 10 is presented

$$R_p = \frac{1}{2.3} \frac{\beta_a |\beta_c|}{\beta_a + |\beta_c|} \frac{1}{I_{corr}}$$
(10)

where, βa — the slope of the anodic curve

 βc — the slope of the cathode curve

 i_{corr} — density of corrosion current ($\mu A / cm2$)

And the corrosion rate was calculated according to ASTM G102-89 (2004) by the following equation

$$CR = K_i \frac{i_{corr}}{\rho} EW \tag{11}$$

where, CR - corrosion rate (mm / year) $K_i - 3.27 \times 10^{-3}$ ρ - material density (g / cm³) EW - equivalent weight (g)

Table 3.9.	Electrochemical test parameters fo	r CoCrFeNiMo _{0.85}	HEA coating in saline a	at
	room tem	perature		

Proba	E _{oc} (mV)	E _{cor} (mV)	i_{corr} ($\mu A/cm^2$)	β_{c} (mV)	β _a (mV)	Rp (kΩxcm ²)	CR (mm/year)
HEA CoCrFeNiMo _{0.85}	-487	-520	0.0011	222.53	140.09	33.980	0.00016

The results of the corrosion test in saline solution of the sample covered with HEA layer by ESD technique resulted in a corrosion rate of 0.00016 mm / year, thus indicating that the material is suitable for aggressive environments such as geothermal. The results of the SEM and EDS microstructural analyses for the sample before testing and after corrosion testing are shown in Figure 3.25.



Fig. 3.25. CoCrFeNiMo_{0.85} HEA coating a) before and b) after exposure to corrosive environment

The results show a series of pores and splashes caused by the ESD deposition technique used for the application of layers, but the pores are present only in the surface layer, the structure not being affected. Due to the possibility of forming BCC structures for this alloy according to VEC calculations, pores are present, even if successive layers of material were applied. A passivation layer can also be observed, which could have been created from chromium segregation according to the results of the EDS analysis.

By comparing the results with previous tests [45], although E_{oc} has a higher electronegativity value than that of the alloy obtained by liquid processing, the corrosion rate value for the CoCrFeNiMo_{0.85} HEA coating tested was lower, due to the fact that a protective film was formed on the surface of the analyzed sample, the coating not being affected as much by the corrosive environment. The high value of electronegativity for the open circuit potential could be caused by the existing pores on the coating surface, due to the fact that passivation occurred over a long period of time. In conclusion, according to the calculation values for the case of corrosion testing of the coating of CoCrFeNiMo_{0.85} alloy with high entropy obtained by ESD deposition technique resulted in a low corrosion rate of 0.00016 mm / year which indicates that this alloy could be used as a protective coating against corrosion in aggressive environments.

3.5. Economic Efficiency of the Coating Obtained by ESD method for the geothermal power plants case

In an article published by Almar Gunnarsson et.al. [46], the effect that geothermal steam has on turbines, which generate electricity, from geothermal stations is analysed. Maintenance costs are directly influenced by factors such as corrosion, erosion, abrasion and deposits, due to impurities in the geothermal steam used [47], resulting in that for a period of 15-20 years, can reach up to 20 million USD [48], for the Hellisheiði geothermal power plant, Iceland, where 7 such turbines are installed [46].

In this case, it was proposed that the covering of the leading edge of the geothermal turbine blades be made on a surface with a width of 20 mm, along its entire length. It was established that the length as the arithmetic mean of the existing dimensions for 50 HZ, presented in equation 12.

$$L_m = \frac{L_1 + L_2 + L_3 + L_4 + L_5 + L_6}{6} \cong 581 \, mm \tag{12}$$
$$S = 581 \, mm * 20 \, mm = 11620 \, mm^2 = 116.2 \, cm^2$$

Hence, it costs \in 54.9 to cover a geothermal turbine blade with an average length of 581 mm. In conclusion, taking into account the purchase price, mentioned above, of a new turbine blade, namely \in 1,164.00, it results that by covering the attack board, in order to avoid the occurrence of defects due to the aggressive environment or corrections or local repairs, could reduce maintenance costs.

GENERAL CONCLUSIONS

The studies for this thesis have been focused on obtaining an alloy with superior properties for highly corrosive environments and relatively low manufacturing costs, which can be used as a coating for equipment and installations already in use. According to the literature and reports presented over the years, the geothermal industry is in a continuous development, due to quantitatively rich resources, with an important spread worldwide, providing low cost services to end users. Although major benefits are associated with this type of energy, the processes of extraction and processing of the geothermal resource, which occur in an aggressive environment, lead to high maintenance costs and frequent repairs. Geothermal steam is mainly composed of H_2S and CO_2 , and in combination with abrasive particles, high pressure and temperatures produce accelerated wear of components that have direct contact with the environment. Because the maintenance costs and the time required for transport and repairs, affect the work efficiency, they led over time, to long research, to obtain a material suitable for this environment, with superior properties, this solution also contributing economically.

For this work the goal was obtain the alloy with high entropy CoCrFeNiMo_{0,85} by the solid state processing, subsequently compacted and processed into electrodes to obtain coatings for use in the geothermal environment. Alloys with high entropy are intensively studied and represent a major point of interest in current metallurgy due to their superior properties compared to classical alloys and their specific effects.

Following the calculation of the valence electron concentration, I decided to select the CoCrFeNiMo alloys with a calculated value of 7.8 and CoCrFeNiMo_{0.85} with a calculated value of 7.86, due to their close values, and in both cases, and the mixture of phases FCC and BCC possibility according to the literature. The advantage of the presence of these phases in an alloy is the increase of its ductility, but also resistance. The graphical representations of the thermodynamic calculations show the obtained close values, which are included in the ranges from literature, for the CoCrFeNiMo0,85 and CoCrFeNiMo alloys.

For the elaboration of the alloy with high entropy CoCrFeNiMo_x, the initial studies and experiments were performed on the alloy obtained in liquid phase. The samples analyses results which were tested in situ for a period of 30 days showed a corrosion rate of approximately 0.00034 mm / year, the structure of the samples not being affected, the effects of steam being present only on the surface of the samples. The favorable results obtained led to the testing of the bulk material in solution with 3.5% NaCl at room temperature, where a corrosion rate of 0.0072 mm / am was calculated, this being a lower value compared to the results for stainless steel tested under the same conditions. Following the results obtained by these first experiments, we obtained electrodes by mechanical processing of the samples and coated stainless steel substrates for testing.

Following the obtaining of the alloy layer with high entropy CoCrFeNiMo, by the presented method, it was analysed from a microstructural point of view. From the analysis of the microstructure of the deposited layer, a homogeneous deposition could be observed, with a certain degree of roughness, which does not affect the efficiency or utility of the deposited layer. The results of the microscopic analyses for the cross section show a good adhesion of the coating deposited to the substrate.

The results of the EDS analysis confirm the composition of the hyperentropic alloy used, but also the fact that during the deposition no oxides or other types of undesired contaminations appeared. From the microstructural analyses and the results of the EDS analysis, we observed the obtaining of a homogeneous deposition. Considering that this

material would be suitable for use in the geothermal environment, we decided that to reduce costs, the production of high entropy alloy should be performed by solid state processing. Starting from raw metallic powders, with a very high purity of Co, Cr, Fe, Ni and Mo, we mechanically alloyed in a humid environment and Argon atmosphere. The alloy was obtained after 30 h of alloying time. The microstructural results SEM and EDS show a high degree of alloying and a good homogenization in the whole mass. No contamination of the material was present and the oxygen content is minimal.

From the characterization of the powder, the slope angle with the value resulted. 19.79 $^{\circ}$ flow rate 4.33g / s and packing ratio 81%, indicated the possibility of further compaction and mechanical processing in the form of electrodes.

The high entropy alloy was pressed with a force of 25 tf and sintered in the furnace, the final samples having a porosity between 20.41% and a density of 6.057 g / cm³ to a porosity of 38.85% and a density of 5.41 g / cm³, values obtained according to the parameters used during the experiments.

The results of the analyses performed on the sintered sample show a good compaction. From the results of the theoretical density calculations obtained before sintering and after sintering in the furnace, the results showed that the minimum porosity value was obtained for the M_P1 sample with porosity of 32.07%, followed by the M_P4 sample with porosity 33.74%. The highest porosity value was obtained for the M_P5 sample, namely 36.7%. This value can be influenced by the lack of binder during pressing, taking into account that the same sintering parameters were used, but also the same amount of material, in the case of both M_P4 and M_P5 samples.

Although the M_P1 sample had the lowest porosity value and the closest to the theoretical density of the CoCrFeNiMo_{0,85} alloy, the parameters of the sintering treatment were not sufficient to obtain a sufficiently consolidated sample, which can be processed later.

The final decision was to continue the experiments with the M_P4 sample, this being sufficiently consolidated for a good handling and mechanical processing in electrodes, for the technique of electrical deposition by sparks. Following the cutting of this sample, there were no breaks or cracks, being suitable for the subsequent mechanical processing in the form of electrodes for deposition.

For the ESD process, electrodes by mechanical processing were obtained, having the dimensions and shape in accordance with the applicator used and the deposition method. The 316 L stainless steel substrate was prepared prior to deposition by sandblasting and cleaning with high purity alcohol. The deposition was made by applying successive layers in the Argon atmosphere, the purpose being to obtain coatings with an increased resistance in intensely corrosive environments.

The microstructural results on the surface, but also in section, present a uniform layer, without major defects and with a good homogeneity, with small surface porosities. The interface area between the layer and the substrate showed no cracks, fissures or pores.

The results of the mapping and EDS analyses confirm the composition of the alloy and the percentage of the elemental materials. It was observed a homogeneous deposition in which the particles are distributed relatively evenly, in which no separation on components or compounds on the entire analyzed surface was highlighted. Although the deposition of the layer was performed in an Argon atmosphere, oxygen is present in the composition, but its amount does not affect the functionality of the coating. The topography shows small surface cracks, specific to this type of deposit, where cooling is very fast. By this deposition method, we obtained a good adhesion, tested by pull off test method, where there were no exfoliations or separations of the layer. The elastic behavior and the moment of epoxy resin yielding during the test result in a better adhesion of the layer to the substrate compared to that of the substrate resin confirmed by the loading-unloading diagram.

The economic efficiency of the proposed method was calculated taking into account the market value of a turbine blade for the geothermal environment. Theoretical calculations have shown that to cover a geothermal turbine blade with an average length of 581 mm we have the cost of $54.9 \notin$. In conclusion, taking into account the purchase price of a new turbine blade, namely \notin 1,164.00, it follows that by covering the board, in order to avoid the occurrence of defects due to the aggressive environment or corrections or local repairs could reduce the costs of maintenance.

ORIGINAL CONTRIBUTIONS

I performed a meta-analysis of high entropy alloys with high corrosion resistance, highlighting the processing methods and properties that can be obtained.

I obtained by two methods of elaboration alloys from the CoCrFeNiMo_x system, namely CoCrFeNiMo by vacuum arc remelting and CoCrFeNiMo_{0.85} by mechanical alloying.

I performed a thermodynamic study for the alloys from the CoCrFeNiMo system with variable molybdenum content.

I have developed a new type of coatings made of CoCrFeNIMo and CoCrFeNiMo $_{0,85}$ by electro spark deposition technique.

The high entropy alloy processing method and the deposition technique were performed following the above mentioned meta-analysis on recent studies in the field, but also following the performance of thermodynamic calculations specific to the studied alloys.

I determined the parameters for mechanical alloying in the mono-planetary mill, in order to obtain a high degree of alloying and a good homogenization.

I studied the evolution of the alloying degree for the high entropy alloy CoCrFeNiMo $_{0,85}$ produced by mechanical alloying.

I determined the pressing curve for the CoCrFeNiMo_{0,85} alloy due to the fact that in literature there is no data available on the processing parameters of the chosen material in metallic powder form. The samples pressing was tested multiple times good result was obtained. For these experiment the parameters such as the feed or pressing force, the mold (to vary the diameter of the final sample), and the binder were varied.

I studied and optimized the final shape of the electrodes used in the process of electro spark deposition process in order to avoid their breaking during deposition.

Another element of originality was the manufacture of the device for testing the adhesion resistance. We managed to obtain a device adaptable to several sample sizes, through a simple principle and with low costs.

I obtained a homogeneous coating, the adhesion of which was also tested with a high corrosion resistance, which can be successfully used for coating turbine blades working in the geothermal environment.

I performed economic calculations to obtain coatings from CoCrFeNiMo0,85 alloy in order to improve the contact surface of geothermal turbine blades.

PROSPECTS FOR FUTURE DEVELOPMENT

The prospects for further development are to improve the deposition process in order to obtain layers with a thickness as uniform as possible. Given that this is a manual process, it will be a real challenge. The size and shape of the layer can also be improved by optimizing the deposition parameters.

I will test the samples deposited with $CoCrFeNiMo_{0,85}$ high entropy alloy by the method electro spark deposition technique by several adhesion tests. Although the results

obtained from the tear test were desirable, I want to discover the critical point at which these layers will develop adhesive and cohesive ruptures.

I also want to test the layers deposited *in situ*, for a better accuracy of the corrosion results, taking into account that the final destination of the layers is the geothermal environment. The results obtained in the geothermal environment of the CoCrFeNiMo samples obtained by the liquid processing method were promising, resulting in further experiments to obtain the alloy by a different processing method in this doctoral thesis.

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RESULTS DISSEMINATION

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- 1. **Geambazu L. E.**, Cosmin C. M., Miculescu F., Csaki I., Mechanical alloyed CoCrFeNiMo_{0.85} high entropy alloy for corrosion resistance coatings, Materials, Volume 14, Issue 14, July 2021
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- 3. Fanicchia, F., Csaki, I., **Geambazu, L.E.**, Begg, H., Paul, S., Effect of microstructural modifications on the corrosion resistance of CoCrFeMo_{0.85}Ni compositionally complex alloy coatings, Coatings, Volume 9, Issue 11, 2019, Article number 695
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Collaborator of research contracts with international participation

- 1. H2020 EU project GeoHex-advanced material for cost-efficient and enhanced heat exchange performance for geothermal application (Grant agreement 851917).
- H2020 EU project Geo-Coat: Development of novel and cost-effective corrosion resistant coatings for high temperature geothermal applications. Call H2020-LCE-2017-RES-RIA-TwoStage (Project No. 764086).

Collaborator of research contracts with national participation

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