

UNIVERSITY POLITEHNICA OF BUCHAREST MATERIAL SCIENCE AND ENGINEERING FACULTY



PhD THESIS

ABSTRACT

RESEARCH ON OBTAINING AND THE PROPERTIES OF HfNbTaTiZr HIGH ENTROPY ALLOY

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Table of Contents

INTRODUCTION
PART I – THEORETICAL STUDIES REGARDING HIGH ENTROPY ALLOYS AND OBTAINING METHODS
Chapter I – Theoretical considerations for high entropy alloys
1. 1. Overview
1. 2. High entropy alloys obtaining methods
1. 3. High entropy alloys corrosion resistance
Chapter II - Mechanical alloying
2. 1. Fundamentals of mechanical alloying
Chapter III - Studies regarding SPS consolidation of HfNbTaTiZr HEA7
Chapter IV – ESD technique
4. 1. Fundamentals regarding electro-spark deposition
PART II – HfNbTaTiZr HIGH ENTROPY ALLOY THERMODYNAMIC STUDY9
Chapter V – Thermodynamic notions
5. 1. Theoretical notions
5. 2. Thermodynamic calculations for HfNbTaTiZr high entropy alloy10
PART III – PERSONAL STUDIES AND EXPERIMENTAL RESEARCH
Chapter VI - Development of high entropy alloys by solid phase method11
6. 1. Development of HfNbTaTiZr high entropy alloy by solid state processing11
6. 2. Metallurgical characterization of metal powders obtained by mechanical alloying14
Chapter VII - HfNbTaTiZr high entropy alloy SPS consolidation18
7. 1. Calculations for the minimum amount of powder required to obtain the samples18
7. 2. Experimental results regarding the consolidation of the HEA by SPS18
Chapter VIII. HfNbTaTiZr high entropy alloy layers deposition by ESD method and analysis by different methods of the obtained coatings
8. 1. The deposition process and coatings obtaining by ESD technique for the studied high entropy alloy
8. 2. Mechanical tests performed on the HfNbTaTiZr obtained coating25
8. 2. 1. Testing the roughness of the samples coated by ESD method25
8. 2. 2. Adhesion resistance testing
8. 2. 3. Hardness measurement results
8. 3. Corrosion resistance testing

REFERENCES	35
RESULTS DISSEMINATION	34
9. 3. PERSPECTIVES FOR FUTURE DEVELOPMENT	33
9. 2 ORIGINAL CONTRIBUTIONS	
	22
9. 1. GENERAL CONCLUSIONS	31
Chapter IX - Final conclusions and original contributions	31

Key words: powder metallurgy, mechanical alloying, high entropy alloys, coatings, electrospark deposition, corrosion resistant, geothermal environment.

INTRODUCTION

High entropy alloys are a relatively new topic in the field of metallurgy, but which is studied in many scientific papers, due to their superior properties and specific effects. The need of developing alloys for aggressive environments in which the costs caused by factors such as corrosion, erosion and more, is a real problem in the industry, thus promoting research focused on surface engineering and improvement by various methods.

The advantages of using high entropy alloys are represented by the possibility of developing materials with established properties, determined by the chemical composition of the mixture, thus resulting in a major improvement compared to conventional alloys.

These alloys can be produced both by liquid state processing methods such as vacuum arc melting or induction melting, solid state processing methods by mechanical alloying, but also other methods according to the field of use.

By mechanical alloying, there is the advantage of obtaining high degrees of alloying and very good homogenization at the molecular level, avoiding unwanted dendritic structures or segregations characteristic of obtaining alloys in liquid state, even when the components have different melting temperatures that can sometimes exceed evaporation temperature of the other elements.

The aim of this doctoral thesis is to obtain an alloy with improved properties, which can be used as a coating in aggressive environments such as geothermal environment, with high resistance to corrosion, erosion and other factors that cause degradation of equipment used in this industry. The study of the literature for this paper was focused on research in the field of high entropy alloys, which highlighted the current research, the effects and properties they have depending on the methods used. The results showed the performance of these alloys that can be a viable solution in different environments, but also their behavior when tested in highly corrosive environments.

Initial research and first contact with the geothermal environment and its effects were carried out by in-situ testing, in extremely corrosive conditions, of the AlCrFeNiMn high entropy alloy obtained by liquid processing. For those tests, the bulk alloy was exposed to geothermal steam in the Rreykjanesbær Power Plant for 30 days. The obtained results showed a high corrosion rate and led to the obtaining and testing of an alloy with a different composition.

For this paper I studied the possibility of developing HfNbTaTiZr high entropy alloy processed in solid state by mechanical alloying in a mono-planetary ball mill, due to the established properties of the alloy, but also according to the results published on this topic. The metallurgical characterization of the alloy confirmed the possibility of further processing.

Due to the high cost of HEAs, an economically efficient method is to coat with this type of alloys. The most known deposition methods are HVOF, LMD, Magnetron Sputtering, PVD and CVD. Another less known method is electro-spark deposition (ESD) being a method that does not induce thermal stress on the covered parts and through which local repairs can be performed as well as surface improvements such as increasing resistance to high temperatures (thermal barriers), increasing wear and corrosion resistance without a major impact on the weight, geometry or production cost of the part.

The aim of the work is to obtain coatings by the ESD method with the HfNbTaTiZr high entropy alloy; coatings intended for use in aggressive environments where corrosion, being a phenomenon that occurs at the interaction between material and environment, has a major negative impact on metallic materials causing damage or failure of parts.

PART I – THEORETICAL STUDIES REGARDING HIGH ENTROPY ALLOYS AND OBTAINING METHODS

Chapter I – Theoretical considerations for high entropy alloys

1.1. Overview

High entropy alloys are currently receiving increased attention from researchers due to their promising superior properties. The fundamental concept of these alloys is based on the diffusion and transformation of the phases that occur. The processing routes for the synthesis of these alloys and the techniques used can be classified into four types (liquid, solid, gaseous or electrochemical processing). Thermodynamic parameters and their contribution to the anticipation of properties are also taken into account. The kinetics of phase transformations are slower than in the case of conventional alloys due to the low speed diffusion that occurs at the complex interactions between the alloying elements and the high activation energy. The competition between the configurational entropy and the enthalpy of mixture is the key factor for determining the phase transformations.

High entropy alloys (HEAs), are alloy systems composed of at least 5 elements in equal or near equal proportions. The principle is based on maximizing the configurational entropy that helps to stabilize the solid solution phases to the detriment of intermetallic compounds. The domain of high entropy alloys is constantly evolving, researchers discovering phenomena that are not fully understood. Their multicomponent nature increases the complexity of the system and the difficulties of analyzing and anticipating their behavior [1].

1. 2. High entropy alloys obtaining methods

High entropy alloys can be obtained by different techniques such as electric melting, Bridgman solidification, mechanical alloying, spraying, laser plating and electro-deposition. The processing path for HEA synthesis can be classified according to the initial state of alloy preparation as follows: liquid, solid, gaseous and finally electrochemical.

Most alloys were produced in the liquid state by electric arc melting, induction melting and Bridgman solidification. During electric arc melting, the electrode temperature can reach 3000 °C and is controlled by adjusting the current. This method is not suitable for low melting point elements such as Mg, Zn or Mn as they can evaporate. In this situation, a suitable method is induction melting. Bridgman solidification or the Bridgman-Stockbarger method is a technique used to obtain mono-crystalline ingots.

Magnetron sputtering and plasma nitriding are among the most popular methods used for gaseous preparation. These techniques are used to obtain thin coatings of high entropy alloys on the surface of the substrate.

The use of the electrochemical method for HEA is limited due to the combination of many electrochemical parameters that affect the anticipated structure. Potentiostatic electrodeposition can achieve a thin layer at low temperature. It was observed that the deposited film has anisotropy and a slightly magnetic behavior. By adjusting the deposition parameters, the thickness and morphology of the structure can be controlled, obtaining high deposition rates. In general, electrochemical deposition is one of the simplest and most efficient methods that allow easy control of nucleation and growth of metal nanoparticles [2].

1. 3. High entropy alloys corrosion resistance

Corrosion is the chemical / electrochemical interaction between the material and the environment and destroys more than three percent of the world's gross domestic product. It is therefore necessary to design materials with a high corrosion resistance.

Going beyond the philosophy of classical alloys, a new class of alloys was discovered, alloys with high entropy. They have unique microstructures made of solid solutions with a random arrangement of multiple constituents, a property that involves a possible increase in corrosion resistance. The impact of corrosion on the proper operation of a material leads to a malfunction during use.

Research on corrosion behavior and the development of corrosion-resistant structural / functional materials is a huge economic benefit. Among the metallic materials, noble metals such as Ag, Au, Pt etc. they have a satisfactory corrosion resistance, but due to their high cost and mechanically poor performance they have a restrictive applicability [3].

Previous research related to the development of corrosion resistant materials has focused on other categories of alloys such as stainless steels, nickel-based alloys, titanium alloys, etc. The principle of elaboration of the listed alloys follows the conventional route by adding alloying elements in relatively low concentrations to a basic element improving the corrosion resistance.

The corrosion behavior of HEAs in various aqueous environments such as saline solution, acids, water at high temperature and pressure has been investigated in the last decade by various researchers [4–9]. HEA-type alloy systems containing passivizing elements such as Cr, Ni, Mo, etc. have demonstrated equivalent or even superior corrosion resistance properties compared to conventional alloys [4, 5].

Moreover, exceptional properties such as strength-ductility combination [10,11], improved fatigue strength [12–14], high breaking strength [15,16] and high temperature stability [17] make HEA the perfect candidate for many industrial fields, especially as superior structural alloys that have a high demand for extreme working environments such as nuclear, for turbines and for the aerospace industry.

Another aspect of the advantage of the corrosion resistance property of HEA is its use in the form of surface coatings. From an economic point of view, the production cost for HEA by electric arc melting is high, taking into account the addition of expensive alloying elements. One solution to this problem is surface coatings.

Recent studies have reported coatings with HEA on substrates of many steels, Al and Si alloys by laser consolidation method [18–21], electro-spark deposition [22], magnetron sputtering deposition [23–25], etc. By using these coating methods a favorable combination of cost and properties was obtained. HEA layers provide protection against corrosion by forming a barrier (stable passivation) against the infiltration of corrosive agents and a high ionic resistivity to minimize electrochemical reactions from under the coating.

The combination of high performance mechanical properties and corrosion resistance of HEAs ensures a remarkable resistance to cavitation-erosion in saline environment [26]. Similarly, the combined resistance to irradiation and corrosion make HEAs a potential candidate for coating materials used in the field of nuclear fuels and high pressure vessels [27]. Moreover, HEA coatings have been reported to have the same composition as the raw material but with superior corrosion resistance properties due to better microstructural homogeneity in the deposited layer [26].

Chapter II - Mechanical alloying

2. 1. Fundamentals of mechanical alloying

Solid state preparation is performed by mechanical alloying (MA), a method that involves cold welding and repeated fracturing of powder particles in ball mills. By mechanical alloying, a variety of alloys can be synthesized, whether or not in a state of equilibrium, starting from mixtures of pre-alloying elements or powders. The process is carried out in three steps: first the powders are homogenized and grinded, after which they are pressed and sintered by a hot isostatic pressing process, and the last step is the heat treatment. It is generally used for turbine blades, aerospace components and a variety of advanced materials with predetermined properties.

Mechanical alloying (Figure 2.1) is a technique used to process metal powders that was developed in the mid-1960s by John Benjamin [28] to produce nickel-based superalloys reinforced with oxide dispersions for gas turbine applications [29]. It was subsequently realized that mechanical alloying can be used for the synthesis of a variety of materials both at equilibrium and outside it at room temperature starting from mixtures of elemental or prealloyed powders. This technique has attracted the attention of researchers in the last 15-20 years.



Figure 2.1. Schematic representation of the mechanical alloying process.

The processing of metallic powders involves repeated cold welding and fracturing of powder particles in a ball mill resulting in the formation of alloy phases. All the unbalanced effects obtained by the rapid solidification process were observed in mechanically alloyed powders, continuously increasing the interest for this technique [30] becoming one of the most popular out-of-equilibrium processing methods.

Being a complex process that involves optimizing some parameters to obtain certain phases, microstructure and / or desired properties, but nevertheless, the nature and composition of the powders will not be taken into account. These parameters influence the nature of the phases formed (solid solution, intermetallic compounds or amorphous phase) in the grinded powder. For an established composition the variables that have an important effect on the final structure on the powder are the following: type of mill used, grinding vial and media, grinding energy / speed, time, weight ratio between powder and balls (BPR), controlled atmosphere, process control agent and grinding temperature. These variables are not completely independent, for example the optimal grinding time depends on the type of mill, the size of the grinding medium, the temperature, etc., the parameters becoming interdependent.

For this work, we used the mono-planetary mill type PULVERISETTE 6 classic line, whose mode of operation is shown schematically in figure 2.2.



Figure 2.2. The mechanical alloying process of the PULVERISETTE 6 ball-mill represented schematically

This mill is composed of a single stainless steel vial and a counterweight to balance the weight distribution during the process. The alloy is made by using stainless steel balls of different sizes.

The preparation of the powder mixture and the preparation of the enclosure for the process took place in an argon atmosphere, for a minimum level of oxidation and to avoid any type of contamination. The parameters for the performed experiments were decided according to the results obtained by several tests.

Chapter III - Studies regarding SPS consolidation of HfNbTaTiZr HEA

The equiatomic alloy HfNbTaTiZr belongs to the group of high entropy refractory alloys [31] with BCC structure [32, 33]. Currently, HfNbTaTiZr ingots are obtained by vacuum arc melting [34-37], processing in vacuum or in a protective atmosphere is necessary due to the high affinity for oxygen of the constituent elements. This type of processing produces materials with a heterogeneous chemical composition and dendritic microstructures [34,35], but by repeated annealing of the cast material, for example during hot isostatic pressing, the homogenization of the microstructure can be obtained [33], but also an unwanted preferential grains orientation.

In contrast to traditional smelting metallurgy, powder metallurgy sintering methods are favorable due to the much lower temperature required for material consolidation [38], offering a significant advantage in the production of refractory metal alloys with high melting points due to high heating rates / cooling, reduced production costs and the possibility of efficient preparation of parts in the form of near-grid. By sintering, homogeneous, dense materials with predetermined microstructures (grain size) can be obtained when the process is optimized [39].

Although obtaining HfNbTaTiZr high entropy alloy has advantages, its production by the SPS method is not sufficiently investigated, so there is very little scientific work [40,41]

in which this method has been tried and the results published. Sintered materials from powders are susceptible to weaker properties compared to molten material, due to the limited cohesion between particles conditioned by the presence of residual porosity in sintered parts, porosity caused by contamination of powders (oxidation). The HfNbTaTiZr alloy exhibits high compressive strength and ductility tested at room temperature in both sintered [32,36] and cast [42]. The cast samples showed a decrease in ductility [35,43] possibly due to the negative effect of micro segregation on the tensile strength properties.

Chapter IV – ESD technique

4. 1. Fundamentals regarding electro-spark deposition

Electro-spark deposition (ESD) is a pulsed micro welding used to repair or improve surfaces. It is based on a capacitor that produces high voltage current pulses for short periods through a consumable electrode that rotates and thus the electrode becomes the anode and the cathode part. When the capacitor energy is released, direct current generates a plasma jet with a high temperature (8000 to 25000 $^{\circ}$ C) between the electrode tip and the part. The plasma jet ionizes the consumable and a small amount of molten material is quickly transferred to the part.

Based on fast pulses, the process does not induce residual temperature or residual stresses of the substrate resulting in non-modification of its microstructure because it remains at room temperature, without thermal distortions or shrinkage. Moreover, the process generates a good metallurgical bond between the deposit and the substrate, which makes this method suitable for repairing worn parts or for improving wear or corrosion resistance. The whole process is carried out under argon shield to prevent oxidation.



Figure 4.1. Schematic representation of the ESD process

The parameters for deposition depend on the type of electrode used, the melting temperature, the thermal conductivity, the chemical reactivity of the anodic elements, the diffusivity, the density, the electrical resistance, the thermal inertia, the flow capacity, and the thermal dependence.

The intensity of the mass transfer and the parameters for deposition may vary depending on the nature of the electrode material and the base material. Energy transfer depends on the physical and chemical characteristics (specific heat, density, conductivity and heat transfer coefficient), the atomic number and the value of the composition of the elements in the cathode, anode and working environment.

The amount of molten and deposited material on the surface depends on various parameters such as: current pulse frequency, distance between electrode and substrate, electrode material properties, average intensity, current voltage, etc. [44].

PART II – HfNbTaTiZr HIGH ENTROPY ALLOY THERMODYNAMIC STUDY

Chapter V – Thermodynamic notions

5.1. Theoretical notions

Prior to the discovery of high entropy alloys, it was believed that combining several elements into an almost equimolar composition would result in a mixture of brittle compounds without any significant technological applicability. Contrary to expectations, these alloys are largely made up of one or a mixture of solid solutions. These phases are FCC, BCC and HCP structures, although they may have severe lattice distortions due to the atomic volume of the constituent atoms.

The microstructure of HEAs can consist of phases of random solid solutions (FCC, BCC), ordered solid solutions (B2, L12) or intermetallic phases (Laves phases). Alloys formed of several elements are considered to form complicated and fragile structures, but contrary to expectations it was found that due to the high entropy of the mixture, HEA type alloys are composed of only a few phases of solid solutions or even a single phase. The number of resulting phases is less than the maximum anticipated number, which is attributed to the increased mutual solubility between elements that prevent the separation into phases of terminal solution or intermetallic compounds.



Figure 5.1. The evolution of the mixing entropy depending on the number of elements

For an arbitrarily chosen composition x, the systems of intermetallic compounds most often have the maximum number of possible phases that can coexist. It is quite rare for an equiatomic multicomponent alloy to have a single phase in equilibrium. When elements combine to form a compound, ΔG , ΔH and ΔS are defined as free energy, enthalpy and entropy of formation. A negative forming energy is thermodynamically favorable for combining elements and forming a compound.

5. 2. Thermodynamic calculations for HfNbTaTiZr high entropy alloy

For this paper I performed the thermodynamic calculations for $Ta_0NbHfZrTi$, NbHfZrTi, $Ta_{0.5}NbHfZrTi$, TaNbHfZrTi, $Ta_{1.5}NbHfZrTi$, $Ta_2NbHfZrTi$ HEAs to establish the influence of the variation of Tantalum content on the thermodynamic parameters, starting from the data published in the literature. The following graphs resulted from the calculations:





Figure 5.2. The results of thermodynamic calculations

The graphs show the increasing trend of the values of the valence electron concentration, the electronegativity difference and the average melting temperature with the increase of the Tantalum alloy concentration. Instead, the average atomic radius decreases as the percentage of Tantalum increases.

Once the Tantalum element is introduced into the alloy, the derivative parameter Ω has a smooth increasing trend with values in the narrow range 12.07-12.87.

Graphical representations of the parameters δ , ΔS_{mix} , ΔH_{mix} indicates that maximum values are obtained, or close to the maximum in the case of ΔH_{mix} , for TaNbHfZrTi equiatomic high entropy alloy.

PART III – PERSONAL STUDIES AND EXPERIMENTAL RESEARCH

Chapter VI - Development of high entropy alloys by solid phase method

6. 1. Development of HfNbTaTiZr high entropy alloy by solid state processing

In order to develop the HfNbTaTiZr high entropy alloy, I opted for mechanical alloying due to the low manufacturing cost, obtaining a high degree of alloying but also an homogeneity throughout the mass of the alloy. Hf, Nb, Ta, Ti and Zr powders with a high purity (> 99%) were used to make the alloy, the particle sizes of which are shown in table 6.1.

Element	Mean particle size (μm)			
Hf	<44			
Nb	75-45			
Та	<65			
Ti	250-149			
Zr	<44			

Table 6.1. Particle sizes of pure metal constituents

In order to have the highest possible efficiency of the mechanical alloying, namely the degree of alloying, but also of the time in which the process takes place, the average particle size must be comparatively close. Figure 6.1 shows macroscopic images of crude elementary powders, and Figure 6.2 shows the results of SEM and EDX analyzes.



Figure 6.1. Macroscopic images of the elemental powders of a) Hafnium, b) Niobium, c) Tantalum, d) Titanium, e) Zirconium





Figure 6.2. SEM and EDS analyzes of elemental powders a) Hf, b) Nb, c) Ta, d) Ti, e) Zr

The equimolar composition of the high entropy alloy was selected because according to the thermodynamic calculations and graphs obtained for the HfNbTaTiZr alloy group, maximum values for enthalpy and entropy of the mixture resulted.

For the experiment, the elemental powders were grinded in a Fritsch planetary ballmill with a single stainless steel vial and balls of the same material. The ratio of balls to powder (BPR) was 10: 1. The process control agent used was N-heptane because it acts as a lubricant and helps during welding and breaking processes during wet grinding, but also to avoid oxidation of powders.

As the selected powders have a high degree of reactivity at ambient temperatures, but also in the presence of oxygen, additional safety conditions were considered. The storage and weighing of metal powders was done in the glovebox because I wanted to obtain an alloy with a low degree of oxidation and made safely. In the glove-box used during the experiments, the oxygen concentration was continuously monitored, the maximum being 2%. Also, the protective atmosphere inside it was high purity Argon.

In the first phase, two sets of samples were obtained milled at different rotational speeds, 200 and 300 rotations per minute, for 125 minutes to determine the optimal speed suitable for this alloy, after which the grinding time was varied from 125 up to 360 minutes. The particle size distribution was measured using a sieving device with oscillations and with screen apertures from 160 μ m to 20 μ m. The sieving is important for the evaluation of the alloying process because the reduction of the particle size can be observed, the average size of the powders being approximately 63 μ m.

I have done a set of samples grinded at 200 rpm which are named as follows: T_0 - homogenized sample, T_1 - 55 minutes, T_2 - 110 minutes, T_3 - 165 minutes, T_4 - 220 minutes, T_5 - 275 minutes. Additionally, a sample grinded at 300 rpm for 180 minutes called T_6 was developed.

Comparative X-ray diffraction analysis for the 7 samples is shown in Figure 6.3. It can be observed how, with the increase of the mechanical alloying time, the present peaks widen and the alloying degree increases as in the case of the sample T6. These powders are alloying with difficulty and it took several attempts to determine a correct alloying time.



Figure 6.3. XRD analysis with wavelength: Cu K-alpha 1.5406 Å

6. 2. Metallurgical characterization of metal powders obtained by mechanical alloying

The powders were analyzed granulometrically to observe the particle size reduction and to determine the appropriate grinding speed for this alloy. The results are shown in Figure 6.4.



Figure 6.4. Particle size distribution of HfNbTaTiZr high entropy alloy obtained at different milling speeds.

The best results on particle size reduction were obtained using the speed of 300 rpm and therefore it was chosen for further experiments. The next varied parameter was the milling time in order to increase the homogeneity and alloying degree, these being unsatisfactory for the grinded sample for only 125 minutes. The name of the samples is as follows: T2 - sample milled 125 min, T3 - 180 min, T4 - 225 min and T5 - 360 min. The microstructures of the samples produced are presented in figure 6.5.



Figure 6.5. Sample microstructures: a. T2, b. T3, c. T4, d. T5 showing the evolution of the composition from inhomogeneous (sample T2) to homogeneous (sample T5)

From the microstructural analyzes it is observed that between the sample T2 and T3 there is a small difference in terms of the degree of homogeneity and particle size. The minor differences between T3 and T4 indicate that with the increase of the grinding time from 180 to 225 minutes small changes result and for this reason it was decided to increase the time to 360 minutes where a significant improvement of the alloying degree was observed and the high entropy alloy obtained is much more homogeneous. Particle agglomerations can also be observed in the T5 sample, due to the ductility property of titanium powder but subsequent processing is not affected [45].

The experiment was extended with the grinding time up to 3300 minutes, the process being interrupted twice to sieve the sample, after 275 minutes and after 1650 minutes. The results of the sieving are presented graphically in figure 6.6.



Figure 6.6. Particle size distribution for samples milled 275, 1650 and 3300 minutes

The results of the particle size distribution indicate that a higher amount of fine powder was obtained in the case of sample H3. The best result in the case of the degree of alloying was obtained after 3300 minutes of grinding at a speed of 300 rpm.

The average particle size of the powders used for the experiments is specified by the manufacturer and has an approximate value of 63 μ m. The comparison regarding the particle size distribution of the initial and the final powder is presented in figure 6.7. A significant reduction in particle size can be observed, which confirms that the experiment was a success; the reason for the failure may be the ductility and coarse granulation of the titanium powder. The value of the average size obtained for HfNbTaTiZr HEA is 27.4 μ m.

The limited information available in the literature on the elemental powders of this alloy, it was agreed to follow the classical method of powder characterization. Due to their reactivity, preventive measures have been taken regarding the handling of powders, this being carried out with increased care in a controlled atmosphere glove-box with an oxygen concentration below 3 percent.

The compressibility index has become a simple, fast and popular method to predict the flow characteristics of powders, being a method of indirect measurement of density, size and shape, surface area, moisture content and cohesiveness of materials because all these can influence the value of the index compressibility.



Figure 6.7. Comparison between the free-flowing and the tap density for elemental powders and the obtained alloy

The graph (Figure 6.7) shows that the alloyed powder has improved characteristics compared to the raw elemental powders.

The flow velocity and slope angle were further measured. These are necessary to check whether the powder meets the conditions necessary for it to be used in deposition processes, meaning that it has a good flow and a slope angle of 35° .



Figure 6.8. Slope angle and flow rate comparison between the elemental powders and the obtained alloy.

For the studied powder, the angle has a value of 17.74° [46]. The flow rate was determined using a Hall calibrated funnel by measuring the time required for a predetermined amount of power to pass through the funnel and the angle of the cone formed by the accumulation of powder.

Chapter VII - HfNbTaTiZr high entropy alloy SPS consolidation

7. 1. Calculations for the minimum amount of powder required to obtain the samples

In order to consolidate the powder to obtain a bulk material from which to mechanically process electrodes to be deposited, calculations were performed to determine the minimum amount of powder.

The purpose is to obtain an electrode with a maximum diameter of 5 mm, this being a necessary criterion for the use of the applicator in the equipment for electro-spark deposition. Losses arising from mechanical processing were also taken into account.

In order to establish the dimensions, the first calculations were focused on determining the theoretical density of the alloy, starting from the densities of the elements, after which the volume of the sample that will result from the SPS sintering process was calculated.

For a density of about 90% of the theoretical one, the required amount of powder was calculated, to which was added 10% representing losses due to the handling of the powders and the grinding of the sintered sample.

7. 2. Experimental results regarding the consolidation of the HEA by SPS

The HEA was sintered into two cylindrical samples with a diameter of 20 mm and a height of 7 mm, using the HfNbTaTiZr powder obtained from the mechanical alloying process. The powders were vacuum processed with an HP D25 spark plasma sintering (SPS) equipment (FCT Systeme GmbH, Germany) in a high density graphite mold with an inside diameter of 20.8 mm with punches of the same material with a diameter of 20 mm, where the inside of the mold was lined with a graphite foil of 0.4 mm thick.

The sintering temperature (T_{sint}) of the powder was 1000 °C, the holding time on the sintering bearing (t_{sint}) was 5 minutes, the heating speed, respectively the cooling speed was 100 °C/min, and the initial pressing force (P_{p-i}) was 15 MPa, while the final pressing force (P_{p-f}) on the sintering bearing was 40 MPa and respectively 50 MPa.



Figure 7.1. Variation of temperature and pressing force over time in the processing of HfNbTaTiZr powders by the SPS process ($T_{sint} = 1000$ °C, $t_{sint} = 5$ minutes,)



Figure 7.2. Macrographic appearance of HfNbTaTiZr samples obtained by the SPS process and mechanically grinded.

Figure 7.2 shows the metallic, uniform, homogeneous and defect-free appearance (cracks or fissures) of the samples obtained from the mechanically alloyed HEA.



11.23% Figure 7.5. SEM and EDS analyses of the sintered sample

18.95%

37.29%

Figure 7.5 reveals a compact structure, without cracks or gaps and EDS analysis confirms the chemical composition of the alloy.

18.14%

14.39%

Sample	H(mm)	nm) Ø (mm) Mass (g) Volume (cm3)		ρ (g/cm3)	m3) Porosity %		
H_P1	7,15	20,38	20,90	2,33	8,96	9,48	90,51
H_P2	7,10	20,40	20,81	2,32	8,97	9,42	90,57

 Table 7.1
 Samples dimensions after sintering

Chapter VIII - HfNbTaTiZr high entropy alloy layers deposition by ESD method and analysis by different methods of the obtained coatings

8. 1. The deposition process and coatings obtaining by ESD technique for the studied high entropy alloy

For the deposition of thin layers by the ESD method of HfNbTaTiZr high entropy alloy, the shown steps in the technological diagram in figure 8.1 are used. After obtaining the samples by mechanical alloying and spark plasma sintered, 316 L stainless steel substrates were prepared for the actual deposition.



Figure 8.1. Technological diagram of the stages prior to deposition

The preparation of the electrodes for the deposition process involves the mechanical processing of the samples from the resulting alloy in order to obtain rods that can be fixed in the clamping system of the applicator.

The coating process is performed in the Argon atmosphere. ESD deposition is performed with Spark Depo Model 300 deposition equipment, with miniature applicator. The miniature applicator is generally used for the deposition of layers with electrodes that have small dimensions, as in the case presented.

The characteristics of the deposited layer are controlled by varying the parameters of the deposition process such as: spark energy, discharge voltage, spark duration, inductance, frequency, temperature, number of passes, electrode pressure applied to the substrate surface, linear speed and electrode rotation speed.



Figure 8.2. Samples of HfNbTaTiZr after the sintering and cutting process in order to obtain electrodes

The preliminary stages of deposition consist in cutting the samples and extracting the central area to have the maximum possible length, followed by mechanical processing. The cutting sample has a square section and because the attachment to the applicator is made in 3 points, the electrode section from the applicator must be circular or hexagonal to facilitate the centering of the electrode and to avoid vibrations during its rotation.



Figure 8.3. The HfNbTaTiZr electrode obtained by mechanical processing used for deposition

Figure 8.4 shows images during the deposition process, and the final sample. For a uniform coating and without surface defects, the deposition was obtained by successive coatings with thin layers of material. Due to the high temperatures during deposition, the electrode was cleaned of the formed oxide layer after each pass.



Figure 8.4. Image taken during deposition and the resulted sample

The high temperatures during deposition are caused by the melting temperatures of the constituent elements of the high entropy alloy, resulting in the need to increase the capacitance and frequency values for efficient deposition. These changes resulted in a slight curvature of the substrate. In order to avoid that, it is necessary to use a substrate with a greater thickness.



Figure 8.5. Substrate samples, the first is as such, the second is sandblasted and the third is coated with HfNbTaTiZr high entropy alloy

Table 8.1 shows the parameters for ESD coating. The configuration of the parameters was decided by testing on several samples, for which we took into account the efficiency of the deposition and the uniformity of the coating.

Material	Substrate	Capacitance Output		Frequency	Atmosphere		
HfNbTaTiZr	316 stainless steel	40µF	100 V	260Hz	Argon (3 l/min)		

Table 8.1. Parameters used for ESD of HfNbTaTiZr high entropy alloy

The analyzes of the surface of the HfNbTaTiZr coating on the stainless steel substrate were performed with the SEM Quanta Inspect S electron microscope, FEI, type FP 201711 with two types of sensors and EDAX Apex. The preparation of the samples for these analyzes consisted of cleaning with high purity alcohol and drying in air flow.





Figure 8.6. SEM and EDS analyses on the coating

From the results of SEM and EDT analyzes it can be observed a homogeneous plateau with areas where there are crusts. Although a network of cracks is present, the result was predictable, considering the deposition method used, where cooling is rapid. The appearance of cracks can also be caused by the coefficient of expansion and contraction of the substrate or by the high hardness of the deposited material. The high temperature during deposition results in the absence of pores on the surface.

The results of the EDS analysis of the surface confirm the composition of the alloy, in which no contaminations are present. Oxygen is present in the composition, although the processes took place in an inert atmosphere of Argon, but its level does not affect the functionality of the deposited layer.

The results of the mapping analyze show a uniform distribution of the elements over the entire surface of the sample, which results in a good homogenization obtained. Niobium and tantalum formed a solid solution and did not present oxides, zonal abundances of these elements being observed in the presented images. Titanium and Zirconium have formed oxides, due to their passivation properties, thus improving the corrosion resistance of the coating.



Figure 8.7. Mapping analysis on the deposited layer

Subsequent tests will consist of trying to improve the deposition process, by changing the parameters or by using a thicker substrate. Deposition on substrates with a different chemical composition can be considered, which can be improved by this method. The aim is to reduce the size of the cracks and eliminate the splashes present. Figure 8.8 shows the optical image of the layer cross-section.



Figure 8.8. The results of the optical analysis of the deposited layer and the highlighting of the layer thickness on the analyzed surface

Non-uniformities can be observed due to the deposition process performed manually, but they can also be influenced by the preparation method, in which there is the possibility of particle extraction. The minimum measured layer thickness is 12 μ m, the maximum measured layer thickness is 28.51 μ m, resulting in an average thickness of approximately 19 μ m.

For SEM and EDS analysis of the cross-section of the deposited sample, after the process of embedding, cutting and surface preparation, the sample was cleaned with high purity alcohol and dried with hot air. The analyzes were performed with the FEI Philips XL30 Envionmental Scanning Electron Microscope and with the EDAX Saphire Energy Dispersive Spectrometry (EDS). Figure 8.9 shows the results of the cross-sectional analyzes of the layer obtained by the ESD method.



Figure 8.9. SEM and ESD analyzes results for the cross-section of the high entropy alloy coating

The results of the SEM analysis confirm the layer thickness of approximately 20 μ m previously measured on the image obtained with the optical microscope, and the chemical composition is confirmed by the results of the EDS analysis. In the chemical composition of the deposited layer, there are no contaminations and oxygen is not present.

Although microcracks and splashes could be observed on the surface of the sample, in the section we could observe a compact, uniform and defect-free layer. There are no gaps at the layer-to-substrate interface, and good adhesion is visible. Successively deposited multiple layers can also be observed, which have formed a compact coating.

8. 2. Mechanical tests performed on the HfNbTaTiZr obtained coating

8. 2. 1. Testing the roughness of the samples coated by ESD method

After obtaining the deposition using the ESD equipment, it was performed a roughness test on the deposited layer. Roughness was measured using a portable Pocket Surf III device. It was performed at least ten measurements starting from the edge towards the center of the sample in the direction of depositing the last layer, as well as transversely on it.

The roughness of the obtained surface can be controlled by varying the deposition parameters, so that in order to obtain a roughness with values as low as possible, the parameters must be reduced, resulting in a lower deposition rate and a thinner layer. During the deposit it was opted for a deposit rate as high as possible.

Table 8.2. Roughness measurement values of the coating						
	Longi	tudinal	Transverse			
	Edge	Center	Edge	Center		
HfNbTaTiZr	(Ra [µm])	(Ra [µm])	(Ra [µm])	(Ra [µm])		
HEA ESD coating on 316L stainless steel substrate	2,99 2,24		2,47	2,69		
	2,28	2,61	2,2	2,02		
	2,9	3,69	2,14	2,87		
	3,1	2,8	3,64	3,67		
	3,07	2,31	2,79	2,99		
Roughness mean value	3,176	2,73	2,648	2,848		

Table 8.2. Roughness measurement values of the coating

From the table it can be observed that the average values on both test directions in the center area of the sample have close values.

According to the SR ISO 468/97 standard [47] regarding the classification of surface roughness into 14 classes, and the average values resulting from the surface of the coated samples fit into class N8 with a roughness between 1.6 and $3.2 \,\mu\text{m}$.

There are no large differences in the values obtained after measuring the roughness on both tested areas, the coating having a relatively uniform roughness with a small difference of up to 1.5 microns.



Figure 8.10. Graphical representation of the values of roughness measurements in the a) Longitudinal and b) Transverse directions

After this test it can be concluded that the roughness in the case of deposits by the method of electro-spark deposition of HfNbTaTiZr high entropy alloy, obtained by mechanical alloying and SPS consolidation, is relatively uniform, without major differences between directions and test areas.

8. 2. 2. Adhesion resistance testing

The samples were glued to the support rod (10 mm diameter threaded rod made of stainless steel) with a two-component epoxy resin with ultra-fast drying and high adhesion resistance. The resistance guaranteed by the manufacturer is 21 MPa.

After gluing, the samples were left for 24 hours for the resin to harden and reach maximum performance according to the information provided by the manufacturer.

The test was performed according to ASTM D4541 [48] and the sample surface was prepared according to ASTM D2651 [49] by mechanical brush cleaning and alcohol wiping. The equipment used is a Walter + Bai Ag LFV-300 kN traction-compression press located in the mechanical testing laboratory belonging to the Faculty of Materials Science and Engineering at the Polytechnic University of Bucharest.

During the test, a constant displacement of 1 mm/min of the piston was performed until the moment of failure, either of the deposited layer or of the resin.



Figure 8.11. Fixing mode of the metal rod to the sample surface in order to test the adhesion

From the image it can be observed the curvature of the coated sample. This curvature occurred during electrical deposition by sparks, but due to the application of the epoxy resin at the interface between the deposited layer and the firing rod, there will be no errors in the results.

In Figure 8.12, the sample adhesion test equipment clamping mode of the device is shown.



Figure. 8.12. Clamping mode of the adhesive strength tester for the sample coated with HfNbTaTiZr high entropy alloy

Figure 8.13 shows the result obtained after testing the adhesive strength of the coated sample. The results show the unaffected surface and the detachment of the epoxy resin from it, without causing exfoliation or rupture of the layer.



Figure 8.13. Results of testing the adhesive strength of the sample coated by electro-spark deposition with HfNbTaTiZr high entropy alloy

At a load of 1.56 MPa, the epoxy resin failed and detached from the sample without exfoliation of the deposited layer. The results are correlated with the graph obtained during the test, represented in figure 8.14. On the graph it can be observed the moment when the resin fails but also its elastic character. The maximum stress applied was 1.56 MPa.



Figure 8.14. Stress chart obtained during adhesion testing of the HfNbTaTiZr coatings

The adhesion test did not produce adhesive or cohesive tears, the adhesion between the deposited layer and the substrate being stronger than that of the epoxy resin [50].

Future tests will focus on establishing the adhesive and / or cohesive layer boundary, even if the results of this test are promising.

8. 2. 3. Hardness measurement results

A method of evaluating the improvement of mechanical properties by coatings can be represented by measuring the hardness. The hardness of the samples, both of the sintered HfNbTaTiZr alloy and of the coatings with it, was measured with a load of 0.98 N with the Shimadzu Vickers hardness tester equipment (Columbia, USA).

The testing was performed at 10 distinct points on the entire surface of the samples, thus obtaining an average value. Comparatively, measurements were also performed on the 316 stainless steel substrate on which the deposition was made. The values obtained in the case of coatings are close to the values obtained for the substrate due to the low thickness of the deposit. The values resulting from the hardness measurement as well as the average values are presented in table 8.3.

Table 8.3. Average values resulted from hardness measurement (HV)					
Material	Average hardness values (HV)	Standard deviation (HV)			
Substrate (316 SS)	250	27,56			
HfNbTaTiZr HEA sintered	840	67,61			
HfNbTaTiZr HEA coating	254	28,20			

The tests performed on the sintered material indicated high hardness values. Jarolav Malek and col. [51] determined the HV hardness on the same type of TaTiHfNbZr alloy obtained by mechanical alloying and sintered SPS obtaining the value of 584 HV. Although the value obtained in this case is a higher one, 840 HV, it can represent the cause of the appearance of the superficial cracks of the deposited layer.

8. 3. Corrosion resistance testing

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One coated sample was tested in an electrochemical cell with saline solution (3.5% NaCl) at an ambient temperature of 25 ± 0.5 ° C in order to monitor the corrosion behavior by the linear polarization technique of the studied high entropy alloy. The equipment used is a Galvanostat / Potentiostat model Ametek PARSTAT 4000 with a saturated calomel electrode (SCE) as reference electrode, a platinum electrode for recording and the investigated sample representing the working electrode.

The corrosion resistance has been tested according to ASTM G5-94 (2011) [52]. The open circuit potential (Eoc) was measured for 6 hours and the Tafel potential dynamic polarization curves were plotted in the range -0.2V + 0.2V with a scan rate of 1mV/s.

The tested coating was very thin, the corrosion resistance being able to be influenced by the deposition thickness. The graphical representation of the evolution of the E_{corr} parameter is presented in figure 8.15 and of the Tafel curves in figure 8.16.





Figure 8.15. Evolution of corrosion potential for HfNbTaTiZr HEA coating



With the aid of Tafel curves, the corrosion resistance characteristic parameters such as: the corrosion potential Ecorr, the density of the corrosion current Icorr, the slope of the cathode curve βc and the slope of the anodic curve βa were determined. By extrapolating the Tafel parameters; the polarization resistance was calculated, a parameter with which the corrosion resistance can be evaluated. Polarization resistance was calculated according to ASTM G59-97 (2014) [53] using the following formula (1):

$$R_p = \frac{1}{2.3} \frac{\beta_a |\beta_c|}{\beta_a + |\beta_c|} \frac{1}{i_{cor}} \tag{1}$$

Table 8.4. Corrosion resistance testing parameters for HfNbTaTiZr HEA coating

Sample	E _{oc} (mV)	E _{corr} (mV)	i _{corr} (µA/cm ²)	β _c (mV)	β _a (mV)	$\frac{R_p}{(k\Omega x cm^2)}$	CR (mm/year)
HEA-H	-183	-244	0,0056	97,68	174,06	48,84	0,00024

The corrosion rate was calculated according to ASTM G102-89 (2004) [54] using the following equation (2):

$$CR = K_i \frac{i_{corr}}{\rho} EW \tag{2}$$

where:

 $\begin{array}{l} CR-corrosion\ rate\ (mm/year)\\ K_i-3.27x10^{-3}\\ \rho\ -material\ density\ (g/cm^3)\\ i_{corr}-corrosion\ current\ density\ (\mu A/cm^2)\\ EW-equivalent\ weight\ (g) \end{array}$

According to the corrosion resistance testing of the sample immersed in saline solution, the coating had promising results considering its low thickness. These results indicate a good electropositive value for the corrosion potential as well as for the polarization resistance, which denotes a desired behavior for this type of coating in corrosive environments. The values obtained in the case of HfNbTaTiZr HEA coating can be compared with the results of testing the 316 stainless steel substrate under the same electrochemical conditions for which a value of -655.6 mV of the $E_{\rm corr}$ parameter was obtained and 12.53 μ A / cm2 for $i_{\rm corr}$ [55].



Figure 8.17. SEM and EDS analysis after corrosion resistance testing

From the analysis of SEM microscopy, traces of the formation of a passivation layer can be observed, also confirmed by the presence of oxygen in the EDS analysis. The cracks appear partially covered, but the SEM image is not very different from the microstructure of the layer before testing for corrosion resistance.

Although the coating shows surface cracks resulting from rapid cooling during the deposition process, the results of the corrosion resistance test demonstrate that they do not affect the performance of the coating. The corrosion rate resulting from the saline solution testing has a very low value (0.00024 mm/year), representing an encouraging result for future tests in much more aggressive environments such as geothermal fluid.

Chapter IX - Final conclusions and original contributions

9. 1. GENERAL CONCLUSIONS

The chemical composition of the studied alloy was established taking in consideration the compatibility between constitutive elements but also the properties they bring to the final alloy.

According to the thermodynamic calculations for HfNbTaTiZr HEA varying the concentration of Tantalum from 0 to 40 atomic percentages, it resulted that for the equiatomic alloy, maximum values for mixing enthalpy and entropy are obtained.

The mechanical alloying was chosen as an elaboration method in order to obtain a high homogenization degree throughout the mass of the material and to avoid segregations and dendritic structures which lead to phase separation.

The powder metallurgy represents an alternative synthesis method to the liquid state processing, representing at the same time a method that involves lower costs excepting the powder prices. Another advantage is the obtaining of finer structures with smaller grain sizes than melting method, effect that can considerably improve the mechanical properties of solid state processed materials.

Spark Plasma Sintering (SPS) was chosen as a consolidation method because higher temperatures and faster heating times can be obtained compared with the conventional sintering, and also a low porosity.

After calculating the chemical composition of the equiatomic alloy, the parameters for mechanical alloying were established following tests in which both the speed and the grinding time were varied in order to obtain the optimal parameters for this alloy.

Handling, weighing and alloying took place in an argon atmosphere to prevent oxidation or ignition of powders. Following preliminary tests, it was determined that the grinding speed should be 300RPM due to the finer granulation results.

Both the elemental powders and the mechanically alloyed powder were metallurgically characterized by sieving to observe the particle size distribution, but also by measuring the flow rate, the slope angle, the free-pouring and the tap density.

According to the analysis of X-ray diffraction on samples extracted during grinding at different time intervals, it turned out that as the grinding time increases, the picks on the diffractograms broaden indicating an increase in the alloying degree and the formation of compounds.

After performing the preliminary tests, the final alloying time was 3300 minutes, the resulting powder being consolidated by the SPS technique. For this step, the sintering parameters were established according to the literature study and calculations were performed to determine the minimum amount of powder required for the final sample to be at least 7 mm thick.

The purpose of the consolidation was to obtain an electrode with a maximum diameter of 5 mm, this being a necessary criterion for the use of the applicator of the electro spark deposition equipment. The losses resulting from mechanical processing were also taken into account. In order to establish the dimensions, the first calculations were focused on determining the theoretical density of the alloy, starting from the densities of the constituent elements, after that, the volume of the sample that will result from the SPS process was calculated. For a density of approximative 90% of the theoretical one, the required amount of powder was calculated, to which was added another 10% representing losses due to the handling of the powders and the grinding of the sintered sample.

Due to the fact that the mold is made of graphite, the phenomenon of carbon diffusion in the sample can occur, this being the main reason why the sample was 2 mm thicker than the size of the electrode.

The HEA alloy was sintered into two cylindrical samples. Sintering was performed at a temperature of $1000 \degree$ C with a holding time on the sintering bearing of 5 minutes and a pressure on the sintering bearing of 40 MPa and 50 MPa respectively. The pressure variation did not have a major impact, the sample pressed with 50 MPa having a 0.06 percent lower porosity than the one pressed at 40 MPa. The consolidated samples had a uniform, homogeneous and defect-free metallic appearance (cracks or fissures).

In order to carry out the deposition process, the median area of the pressed sample at 50 MPa was cut to have the maximum possible length and mechanically processed in order to obtain the deposition electrode. In order to shorten the time required for mechanical processing, only the electrode holding area in the applicator and the opposite end were machined, the central area remaining unprocessed providing increased mechanical resistance against shearing.

The parameters of the deposition process were established by repeated tests until a satisfactorily higher deposition rate and a thicker layer were achieved.

The samples were deposited by repeated passes, after each pass changing the direction of deposition to 90 $^{\circ}$. The microscopic analysis results of the cross-section deposited sample indicate a relatively uniform layer with small superficial cracks.

The roughness of the obtained layer was measured starting from the edge towards the center of the sample in the direction of depositing the last layer, as well as transversely to it.

The average values resulted indicates a relatively uniform roughness without major differences between directions and test areas, the difference being a small one of up to 1.5 microns.

After that, the coating was also subjected to a pull-off test to determine its adhesion to the substrate. The adhesion test did not produce adhesive or cohesive tears, the adhesion between the deposited layer and the substrate being stronger than that of the epoxy resin.

The hardness of the samples, both of the sintered HfNbTaTiZr alloy and of the coatings with it was performed in 10 distinct points on the entire surface of the samples, obtaining in this way an average value. Comparatively, measurements were also performed on the 316 stainless steel substrate on which the deposition was made. The values obtained in the case of coatings are close to the values obtained for the substrate due to the low thickness of the deposit. The tests performed on the sintered material indicates high hardness values of up to 840 HV, probably representing the cause of surface cracks in the deposited layer.

According to the corrosion resistance test for sample immersed in saline solution, the coating had promising results considering its low thickness. These results indicate a good electropositive value for the corrosion potential as well as for the polarization resistance, which denotes a desired behavior for this type of coating in corrosive environments. The values obtained in the case of HfNbTaTiZr coating can be compared with the results of

testing the 316 stainless steel substrate under the same electrochemical conditions for which a value of -655.6 mV of the E_{corr} parameter was obtained and 12.53 2A / cm² for i_{corr} .

Although the coating shows surface cracks resulting from rapid cooling during the deposition process, the results of the corrosion resistance test demonstrate that they do not affect the performance of the coating. The corrosion rate resulted from the saline test has a very low value (0.00024 mm / year), representing an encouraging result for future tests in much more aggressive environments such as geothermal fluid.

9. 2 ORIGINAL CONTRIBUTIONS

I performed a thermodynamic study for the alloys in the HfNbTaTiZr system, through which I highlighted the influence of Tantalum content

I studied the evolution of the alloying degree for the high entropy alloy HfNbTaTiZr, for which I obtained a high alloying degree after several tests performed.

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.

After the consolidation of the metal powder and the mechanical processing in the form of electrodes from the sintered alloy, I optimized their shape, in order to improve the electro spark deposition.

This deposition method has not been used in the deposition of high entropy alloys and being an element of novelty, it resulted in the lack of bibliographic references for this process. The deposition parameters were decided after multiple tests and adjustments, thus managing to obtain coatings with superior properties. By obtaining these coatings I observed superior qualities and properties, the coatings being suitable for aggressive environments with high corrosion.

Another element of originality is represented by the manufacturing of the adhesion test device through which we could test the adhesive strength of the layers, this rig being also adaptable to other sample sizes.

The tests performed for this paper showed the obtaining of the initially proposed coatings, and it will contribute to improve the processes.

9. 3. PERSPECTIVES FOR FUTURE DEVELOPMENT

Further development will focus on optimizing the deposition process in order to obtain uniform and crack-free coatings. Although this process is prone to the presented types of defects, the reduction of their number could be achieved by depositing the layers on substrates with a greater thickness, thus avoiding the deformation.

I also want to test the adhesion of the layer to the substrate by the Scratch Test method and by Bending Test. Although the results of the adhesive strength test of the coated samples were conclusive, the results will be completed by knowing the maximum limit of cohesive or adhesive strength.

Another development perspective is represented by in-situ testing of corrosion resistance in geothermal environment. The geothermal environment is known for high corrosion, caused by various factors. Taking into account the results of previous testing in this type of environment, I want to test the deposited layers in order to obtain important results.

Last but not least, I want to test this alloy in simulated body fluids taking into account that the constituent elements of the HfNbTaTiZr high entropy alloy have biocompatibility properties, and the alloy showed high resistance under corrosive conditions.

RESULTS DISSEMINATION

Articles Published in Web of Science Journals in the Doctoral Thesis Field with Impact Factor

- 1. **C A Manea,** M Sohaciu, R Stefănoiu, I M Petrescu, M V Lungu, I Csaki, New HfNbTaTiZr high entropy alloy coatings produced by electro spark deposition with high corrosion resistance, Materials, 2021, Accepted for publication.
- 2. Karlsdottir, S.N., Csaki, I., Antoniac, I.V., **Manea, C.A.**, Stefanoiu, R., Magnus, F., Miculescu, F. Corrosion behavior of AlCrFeNiMn high entropy alloy in a geothermal environment, Geothermics Volume 81, September 2019, Pages 32-38

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 Geambazu L.E., Manea C. A., Csaki I., Karlsdóttir S. N., High Entropy Alloys in Geothermal Environment, In Proceeding of International Scientific Conference On Advances In Mechanical Engineering 12-14 October 2017, Debrecen, Hungary, pg 158-161

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).
- 2. 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

1. Fondul Social European – POCU "Sisteme de învățare bazate pe muncă prin burse antreprenor pentru doctoranzi și postdoctoranzi (SIMBA)", Programul Operational Capital Uman, Contract nr. 51668/09.07.2019, cod SMIS 124705.

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