National University of Science and Technology
POLITEHNICA Bucharest
Material Science and Engineering Faculty
MATERIAL SCIENCE AND ENGINEERING DOCTORAL SCHOOL
Department of Metallic Materials Science and Physical Metallurgy

PhD THESIS

ABSTRACT

STUDIES AND RESEARCH ON COATINGS OBTAINED FROM HIGH ENTROPY ALLOYS PRODUCED BY SOLID STATE PROCESSING FOR BIOMEDICAL APPLICATIONS

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INTRODUCTION

High entropy alloys, abbreviated as HEA, are a relatively new toopic in materials engineering, being introduced by J.W Yeh and his collaborators in 2004 [1.1], the studies in the field being continued and disseminated by authors such as B. Cantor, I. Chang and others [1.2] until the present days.

This new class of alloys is of great interest in modern metallurgy due to the possibility of obtaining materials with predetermined properties depending on the chosen chemical composition, the variety of methods of obtaining that can start from all states of aggregation, the results leading to the fulfilment of the final goal of applicability in many fields.

The main aspects pursued since the beginning were directed towards superior properties such as wear and corrosion resistance, high hardness, high temperatures resistance and biocompatibility properties, all being determined by the specific effects of HEA.

The main goal of this doctoral thesis was to obtain a high entropy alloy with superior properties, in the form of a metallic coating, which can represent a solution for improving the surface of the equipment used in the biomedical field by solving the problems of corrosion and wear that are frequently encountered.

The doctoral thesis is divided into two main sections, namely **PART I** - THEORETICAL STUDY OF ALLOYS WITH COMPLEX COMPOSITION FOR AGGRESSIVE ENVIRONMENTS WITH POTENTIAL BIOMEDICAL APPLICATIONS and **PART II** - STUDIES AND PERSONAL EXPERIMENTAL RESEARCH.

Part I includes the theoretical studies that were the basis of this research, in which the theoretical aspects regarding high entropy alloys, methods of obtaining the metallic powder material, compaction, sintering and deposition of protective coatings were taken into account. Also, the theoretical study includes the current state of research in the field of these alloys, representing a starting point for the research carried out. Taking into account the novelty of this topic, the references from the literature regarding the studied alloy were limited, thus requiring multiple attempts regarding the establishment of the development parameters, the testing techniques for the obtained materials and the detailed analysis of the materials both from a microstructural and chemical point of view in order to describe the phenomena that occur along the way.

Part II of the thesis includes the experiments carried out during the years of study, which were the basis for obtaining high entropy alloy coatings with possible biomedical applications, being completed by microstructural and chemical analyzes carried out for each stage of the study.

In this doctoral thesis, the research was focused on the solid state processing of high purity **cobalt, chromium, molybdenum, niobium** and **titanium** powders with the aim of developing the **CoCrMoNbTi alloy** that exhibited a high degree of alloying and homogeneity. The advantage of mechanical alloying is that it does not lead to the formation of unwanted dendritic structures or segregations, which are often present in the case of liquid processing methods (eg vacuum arc melting).

The component elements were chosen according to their particular properties such as resistance to corrosion and wear, but they all had one main point in common, namely biocompatibility to make their application in the medical field possible. Also, the chemical composition of this material took into account the results of thermodynamic calculations that indicate the theoretical properties and describe the specific characteristics of HEA.

After the development of the alloys in the form of metallic powder, it was technologically characterized regarding the flow rate, the free flowing density, the tapped density, the slope angle and the packing density. These parameters are necessary to determine the compatibility of the powder with spraying deposition equipment (flow rate), where a powder that does not flow well can damage the installation. The free flowing density provides data on the volume occupied by the uncompacted powder and the tapped density indicate the compaction capacity of the material and the final density. The degree of packing indicates the efficiency of the material's compressibility.

According to the obtained results, spark plasma sintering (SPS) was selected as consolidation method, this method being economically efficient due to considerations such as short process duration, minimal losses and advantageous regarding the high sintering temperatures, compaction up to 99% of the theoretical density and a very low degree of porosity. The presented results highlighting the efficiency of this method.

The sintered samples were prepared metallographically by polishing with abrasive paper with different grits and cleaning with high purity alcohol. After sintering, the ideal candidate for obtaining electrodes was selected, the sample being mechanically processed with the necessary specifications for the electro spark deposition (ESD) equipment applicator.

In order to achieve coatings with possible biocompatible properties, the electro spark deposition method was used due to the economic efficiency that this technique offers both in terms of very small material losses and low energy consumption.

During the research, starting from the powder material until obtaining the coatings, microstructural and chemical analyzes were carried out to check and, if necessary, adjust the parameters of the processes, but also for the early observation of the presence of impurities and contaminants in the composition. The obtained coating was analyzed both on the surface and in the cross section for a better understanding of the phenomena that occurred and to draw some correct and relevant conclusions.

The mechanical testing of this coating consisted in testing the adhesion of the coating to the substrate using the Pull Off Testing technique. This analysis provides essential data for establishing functionality in work conditions.

Following all the results obtained during this research, corrosion testing was carried out in a relevant biocompatible environment, i.e. simulated body fluids (SBF).

In addition to the main parts of this thesis, namely the theoretical study part and the research itself, this thesis includes chapters related to original contributions and future development perspectives, which finalize and express the possibilities of continuing research in the chosen field for improving the results.

PART I - THEORETICAL STUDY OF ALLOYS WITH COMPLEX COMPOSITION FOR AGGRESSIVE ENVIRONMENTS WITH POTENTIAL BIOMEDICAL APPLICATIONS

CHAPTER 1 - Effects of Corrosion and Wear in the Biomedical Field

Surgical instruments are essential resources for any surgical unit. Their quality is crucial for the efficiency of the operating room and the safety of patients. A quality reprocessing of surgical tools reduces their wear, thus ensuring increased durability. Implementation of guidelines formulated for methods of reprocessing and sterilization of surgical instruments is of major importance. This aspect is particularly relevant in developing countries where resources are limited and where such practices can reduce medical costs.

1.1. Corrosion of prostheses and medical instruments

Damage patterns of general surgical instruments

The most common observations were stains, present in 97.87% of instruments, followed by component loosening in 82.97%, rust in 27.65%, pitting in 25.5%, and misalignment in 19% of instruments. [1.3]. Examples of defects caused by corrosion in the case of medical instruments are shown in figure 1.1.

Figure 1.1. *Corrosion effects on medical instruments. Images belong to Munakomi S, Shah R and Shrestha S. 2018, 7:102 [1.3]*

Damage patterns of neurosurgical instruments

The most common observations were stains, found in 38.29% of instruments, followed by component loosening in 31.91%, misalignment in 29.78% and discoloration in

23.4%. For joints, loosening and tarnishing were observed in 29.78% of instruments, while rust was present in only 8.5%. Fractures were observed in 27.65% of instruments, with the majority being at the tip (46.1%), followed by joint in 23% and shaft and handle in 15.38% each. [1.3]

1.2. Orthopaedic implants and the advantages of titanium alloys

Metallic materials, which have the oldest history compared to other types of materials such as ceramics and polymers in terms of their use for biomedical purposes, exhibit more reasonable mechanical properties than ceramics and polymers. In the case of orthopaedic implant applications, allergic reactions are estimated to occur in 1% to 5% of patients. The effects of corrosion on implants are shown in figure 1.2.

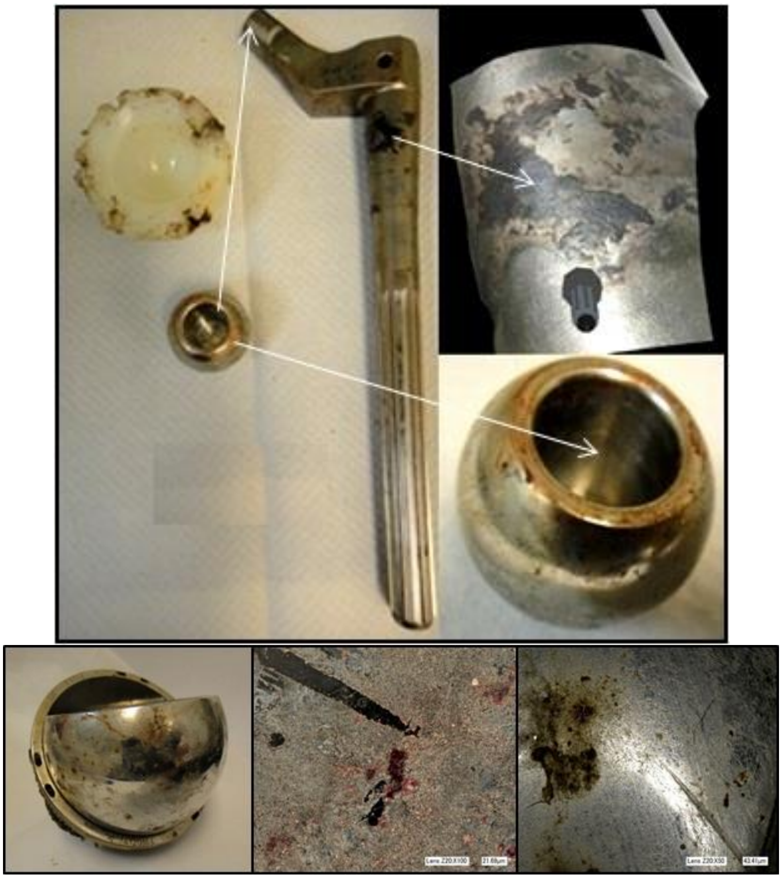


Figure 1.2. *Corrosion effects in the case of implantable components.*
Images belong to The BONE Lab (Biomaterials for Osseointegration and Novel Engineering) 2024

CHAPTER 2 – Theoretical study regarding the high entropy alloys

Taking into account the types of effects that appear in the biomedical field caused by the environment (body fluids) that cause the appearance of corrosion and wear (caused by prolonged use) on the instruments or the implanted prostheses, the researches were directed towards finding an optimization solution of them either through new materials or coatings with superior properties. In this way, high entropy alloys were taken in consideration due to their specific effects, but also to the predefined properties that can be customized according to the needs or the final application.

2.1. Theoretical considerations for high entropy alloys

High entropy alloys, also known as multi-component alloys (MPEAs), are alloys composed from five or more elements and can be obtained by different techniques, exhibiting unique effects and remarkable properties. Compared to HEAs, traditional alloys are generally composed of one or two main components chosen for their distinct properties and to which alloying components are subsequently added to further improve the properties.

From the literature studies and previous research [1.27], it was observed that high entropy alloys (HEA) exhibit the following main characteristics:

1. High entropy: This contributing to the simplification of the microstructure, resulting mainly in solid solution phases with face-centered cubic (FCC) and body-centered cubic (BCC) structures.
2. Severe deformation of the crystalline structure: This deformation significantly influences the mechanical, physical and chemical properties of the alloys.
3. Slow diffusion: Leading to the formation of nanocrystalline or even amorphous structures.
4. Random mixing effects ("cocktail effect"): Interactions between the various component elements give unique properties to HEA alloys.

The high entropy effect [1.25] suggests that a disordered solid solution can be stabilized if the entropy is high enough, reaching maximum values at equimolar or near equimolar ratios of the constituent elements, being essential for the formation of HEA alloys.

The slow diffusion effect [1.25] suggests that the kinetics of transformations in HEA is much slower compared to conventional systems. This is partly caused by the increased activation energy required for substitutional diffusion and partly due to atomistic phenomena that ultimately slow down the diffusion process.

Phase transformations that depend on the diffusion of atoms require the cooperative movement of elements to achieve a balanced distribution between phases. This, together with the deformation of the crystal lattice that obstructs the movement of atoms, significantly reduces the effective diffusion rate in the HEA.

The severe lattice distortion effect [1.25] is largely determined by the different atomic sizes specific to each constituent element in the high-entropy alloy. In high entropy alloys (HEA) each atom in the multicomponent matrix is surrounded by other types of atoms, and thus stresses arise mainly due to differences in the size of the atoms, leading to a deformation of the crystalline network.

The cocktail effect [1.25] is used to improve the properties of alloys composed of at least five main constituent elements. The alloy may contain one or more phases, depending on the composition and the elaboration process.

The core effect improves HEAs by giving them superior properties that can make them useful in a variety of applications. The BCC single-phase crystalline structures show high yield strength due to pronounced solid solution hardening, while FCC single-phase crystalline structures are known for their increased ductility.

2.2. High entropy alloys obtaining methods

In the case of high-entropy alloys, kinetics plays a crucial role in determining the crystallographic phases. The microstructure of the alloy can be directed by controlling the cooling rate during solidification, the type of processing applied and the plastic deformation, in combination with various subsequent heat treatments. In this way, the properties of the alloy can be optimized by adjusting the processing parameters.

The synthesis process of HEA can be classified according to the initial state of preparation of the alloy, whether it is liquid, solid or gaseous. Various processing techniques such as electric arc melting, Bridgman solidification, mechanical alloying, sputtering, laser plating and electro spark deposition (ESD) can be used to produce high entropy alloys. [1.31]

2.3. Theoretical considerations regarding biocompatible high entropy alloys (Bio-HEA)

Nova et al. [1.32] developed CoCrMoE5Ti alloys by casting and spark plasma sintering and studied the microstructure, mechanical and tribological properties of the developed alloy. They found that the addition of Ti to the CoCrMo alloy significantly improved its wear resistance. This demonstrates that the addition of Ti to the CoCrMo alloy through adequate processing can be beneficial in developing a better material for knee implants.

Conventional manufacturing processing such as casting, machining, forging, and forming have been used to fabricate knee implants, but the fabricated implants have poor surface quality and mechanical properties [1.33, 1.34]. Moreover, these processes are inflexible for manufacturing prostheses in near-final form and productive of complex customized shapes.

Chapter 3. - Fundamentals of Mechanical Alloying and Spark Plasma Sintering (SPS)

Mechanical alloying is a process in which powders of relatively equal size of the constituent elements are mixed in an enclosure together with grinding balls. They are subjected to the grinding process for a certain period of time, with the aim of obtaining a solid alloy in which each particle of the powder will contain all the elements initially added to the composition.

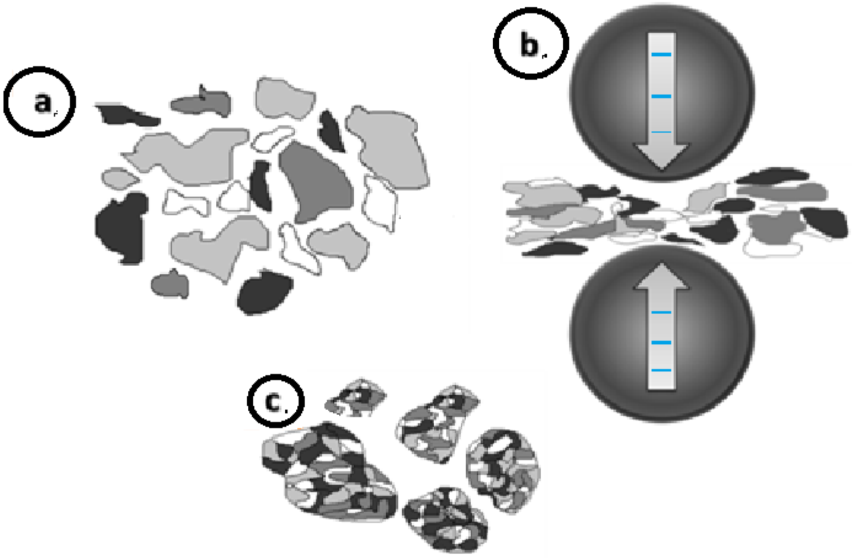


Figure 3.1. *Mechanical alloying graphic representation*

During this process, the particles are subjected to flattening, fracturing and rewelding due to repeated collisions between the grinding balls. These interactions lead to the formation of new shapes and surfaces, phenomena encountered in all types of powders that go through the mechanical alloying process [1.55].

In the mechanical alloying technology, there are three possible combinations of powders:

1. **Ductile – ductile combination:** This is considered ideal for mechanical alloying. In this case, small amounts of the powder mixture tend to weld together and form a protective barrier in the enclosure from the start of the process. Ductile particles flatten during the process, forming lamellar structures from the initial mixture.
2. **Ductile – brittle combination:** In this scenario, brittle particles such as oxide particles are dispersed in a ductile matrix. In the first part of the process, the collision of the grinding balls leads to the flattening of the ductile particles and the fragmentation of the brittle particles.
3. **Brittle – brittle combination:** This type of combination involves the dispersion of brittle particles in a similar brittle matrix. During mechanical alloying, brittle particles embed themselves into less brittle particles. This combination can lead to the formation of amorphous phases, intermetallic and solid solutions at the atomic level, with a structural refinement influenced by the mechanical energy generated during the process (figure 3.4.) [1.56].

3.1. The mechanical alloying process variables

Optimizing the parameters in the mechanical alloying process is essential to obtain the desired phase, microstructure or final product. The parameters with major impact in achieving these objectives include:

- **Type of mill used in the process**: Mills can be of various types, each having different influences on the grinding process and final results.
- **Type of enclosure**: The choice of enclosure can influence the grinding conditions, temperature distribution and material behavior during the process.
- **Effective grinding time and grinding speed**: These parameters determine the degree of particle deformation and refinement during the process.
- **The size and type of balls used in the process**: The grinding balls affect the efficiency of the grinding process and the degree of mixing of the powders.
- **Ball-to-powder mass ratio**: This ratio influences the density and efficiency of the grinding process.
- **Degree of powder and ball filling of the enclosure**: Adequate filling of the enclosure with powder and balls ensures a uniform and efficient process.
- **Atmosphere and process control agent**: Atmosphere and the use of a control agent can influence chemical reactions and oxidation of materials during the process.
- **Temperature at which grinding occurs**: Temperature can affect chemical reactions, oxidation reactions and material behavior during the mechanical alloying process.3.2.

3.2. The consolidation of the metallic powders by Spark Plasma Sintering technology

Electric Field Assisted Sintering (SPS) is an innovative technique that stands out for extremely fast heating times and processing cycles.

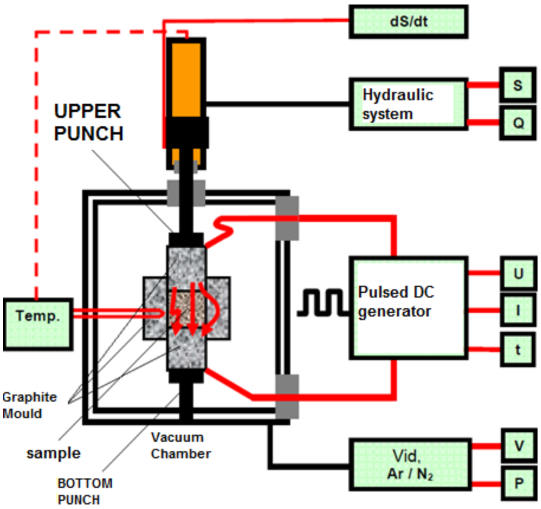


Figure 3.6. *Operating scheme of the SPS equipment [1.77].*1

At the contact points of the powder particles, processes such as Joule heating, plasma formation and electron migration take place, allowing the use of reduced pressures and temperatures compared to classical sintering or hot pressing [1.76].

Chapter 4 - The use of materials as coatings for surface enhancement

Deposition of thin layers involves coating metallic or non-metallic surfaces with high-performance materials, with the aim of improving the properties of parts made from common materials. This method is economically preferred because it allows the use of expensive materials only for the coating layer, instead of the entire part being manufactured from expensive material, thus reducing energy and resource consumption. Thin layers have a significant impact on the physical properties and behavior of the material [1.54].

These layers are essential in various modern technologies, including gas sensors, infrared detectors, solar cells, interference filters, polarizers, superconducting layers, anti-corrosion coatings, etc. The deposition process is influenced by the substrate cleaning methods, the deposition technique used and the thickness of the applied layer. Thin film deposition techniques can be classified as follows:

4.1. Fundamentals regarding deposition techniques

Materials science and engineering innovations have brought beneficial changes to modern society, enabling the development of new materials with outstanding chemical, physical and mechanical properties. Contemporary technology relies on thin layers for various critical applications [1.80]. The use of the optical properties of metallic layers and the scientific interest in the behavior of two-dimensional solids have stimulated intense research in this field. These studies have propelled new areas of research in the physics and chemistry of materials, exploring unique phenomena related to the thickness, geometry and structure of thin layers [1.80].

4.2. Coating techniques for properties enhancement

The deposition of layers can be achieved by various methods, each with its own advantages and specific applications:

1. Chemical Vapor Deposition (CVD): Uses chemical reactions to deposit a thin layer of material on the surface of a substrate.
2. Physical Vapor Deposition (PVD): Uses physical processes, such as evaporation and ion bombardment, to deposit thin layers.
3. Chemical Deposition: It involves chemical reactions in solution to deposit thin layers on the substrate.
4. Thermal spraying (HVOF – High Velocity Oxygen Fuel): A layer is applied by projecting molten particles at high speeds.
5. Laser cladding (Laser Cladding, Laser Metal Deposition): Uses a laser beam to melt and deposit material on the surface of a substrate.
6. Atomic Layer Deposition (ALD): A thin layer is built up atomically layer by layer, ensuring precise thickness control.
7. Electrical Spark Deposition Coating: A thin layer of material is deposited by electrical discharges

4.2.7. Electro Spark Deposition (ESD)

Electrospark Deposition (ESD), also known as micro-arc welding, is a technique that involves pulsed micro-welding and is used to repair or improve surfaces. The equipment works on the basis of capacitors that produce discharges of high-intensity current pulses at short time intervals between the anode, represented by the consumable electrode, and the cathode, represented by the substrate. The energy from the discharge of the capacitors generates a jet of very high temperature plasma between the electrode and the workpiece producing a small amount of molten material that is transferred from the electrode to the substrate.

The advantage of this deposition technique is represented by the robust metallurgical bond that forms between the deposited material and the substrate, being a viable method for performing local repairs or for improving the corrosion or wear resistance properties of the surfaces affected by these phenomena [1.81, 1.82]. In figure 4.2. can be observed how the spark is formed on the surface of the substrate, resulting in the actual deposition of the material.

Figure 4.2. *Electrodeposition process using the miniature applicator* [2]

PART II - STUDIES AND PERSONAL EXPERIMENTAL RESEARCH

Chapter 5 - Development of CoCrMoNbTi high entropy alloy by mechanical alloying

5.1. Thermodynamic study regarding CoCrMoNbTi high entropy alloy

Alloys with high entropy present unique properties due to the formation of solid solutions, according to bibliographic data [2.1-2.7].

For this work, the thermodynamic calculations were made for CoCrMoNbTi HEA, in table 5.1. showing the properties of the component elements of the studied alloy, and table 5.2 showing the mixing enthalpy of the binary pairs using the model made by Miedema et al. [2.1].

***Table 5.1**. The properties of the constituent elements of the studied high-entropy alloy*

Element	**Atomic No.**	**R (Å)**	**Electronegativity**	**VEC**	**T_m (°C)**	**c_i**
Co	27	1,670	1,88	9	1.495	0,2
Cr	24	1,850	1,66	6	1.857	0,2
Mo	42	2,010	2,16	6	2.617	0,2
Nb	41	1,429	1,60	5	2.468	0,2
Ti	22	1,462	1,54	4	1.668	0,2

***Tabelul 5.2.** Enthalpy of mixing of binary combinations of high-entropy alloy components, based on the model of Miedema et al. [2.1]*[1]

-	**Co**	**Cr**	**Mo**	**Nb**	**Ti**
Co	-	-4,5	-4,9	-24,5	-28,3
Cr	-4,5	-	0,4	-7,2	-7,5
Mo	-4,9	0,4	-	-5,7	-3,6
Nb	-24,5	-7,2	-5,7	-	1,97
Ti	-28,3	-7,5	-3,6	1,97	-

After performing the calculations, it can be observed that for the alloy studied in this thesis, the resulting values are within the ranges established by theory regarding the mixture enthalpy and mixture entropy. Although in this case the difference in atomic size is greater than the one specified theoretically, this aspect can result in a greater hardness of the material, respectively a greater resistance to wear.

From a mechanical point of view, the alloy falls within the established conditions, to be tested after the actual elaboration.

5.2. Mechanical alloying and characterization of the high entropy alloy powder

The development of the high-entropy alloy in the form of metal powder was carried out with a Fritch mono-planetary mill model PULVERISETTE 6 classic line (figure 5.1) with counterweight. Mechanical alloying involves obtaining a high degree of alloying and homogeneity of the processed material, this technique being superior to other alloying methods from this point of view (ex. liquid alloying).

(a) (b)

Figura 5.1. *Fritsch® Pulverisette 6 Classic Line a) planetary mill and b) Stainless steel vial and balls.*

Mechanical alloying can also be described as a synthesis technique where the elementary materials in solid state are in a repetitive process in which they are cold welded, fragmented, and agglomerated, thus obtaining the actual alloy.

The evolution of the degree of alloying was monitored by taking samples from the mixture once every 6 hours. To reduce the degree of contamination and oxidation that could occur during alloying, the enclosure was flooded with high-purity argon.

Due to the improvement of the alloying efficiency and the decrease of the possibility of adhesion of the metal powder to the grinding medium (enclosure, balls), wet grinding was carried out, with 2 mass% N-heptane (as a process control agent - PCA). The alloying process parameters used were: grinding speed of 300 RPM with 10:1 BPR (balls to powder ratio) for a period of 30 hours to achieve the highest degree of alloying. During mechanical alloying, breaks were necessary to avoid overheating and excessive welding of the particles.

In order to verify the degree of alloying, the morphology of the powders, the chemical composition and the distribution of particles (mapping), analyzes were carried out with the Tescan Vega II-XMU SEM equipment coupled with the EDS detector Bruker xFlash 6/30, the same equipment that was also used for the analysis of the morphology of the powders in pure state. The results of the microstructural and chemical analyzes are presented in the following figures.

Figure 5.3 shows the results of the microstructural and compositional analyzes for the homogenized sample. For a better distribution of the particles in the mixture, the component materials were homogenized in the planetary ball mill for 30 min, followed by the collection of a sample for analysis. As can be seen, the particles have different shapes and sizes, and the EDS analyzes confirm the composition without contamination, the oxygen being below the detection limit of the equipment.

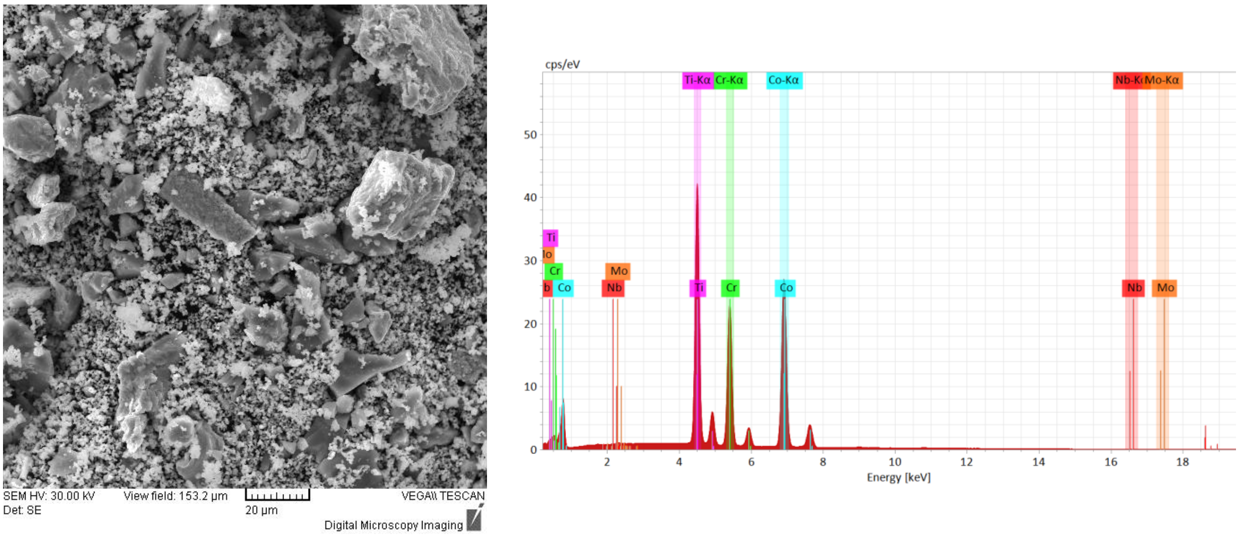


Figure 5.3. *The results of the microstructural and compositional analyzes of the homogenized mixture*

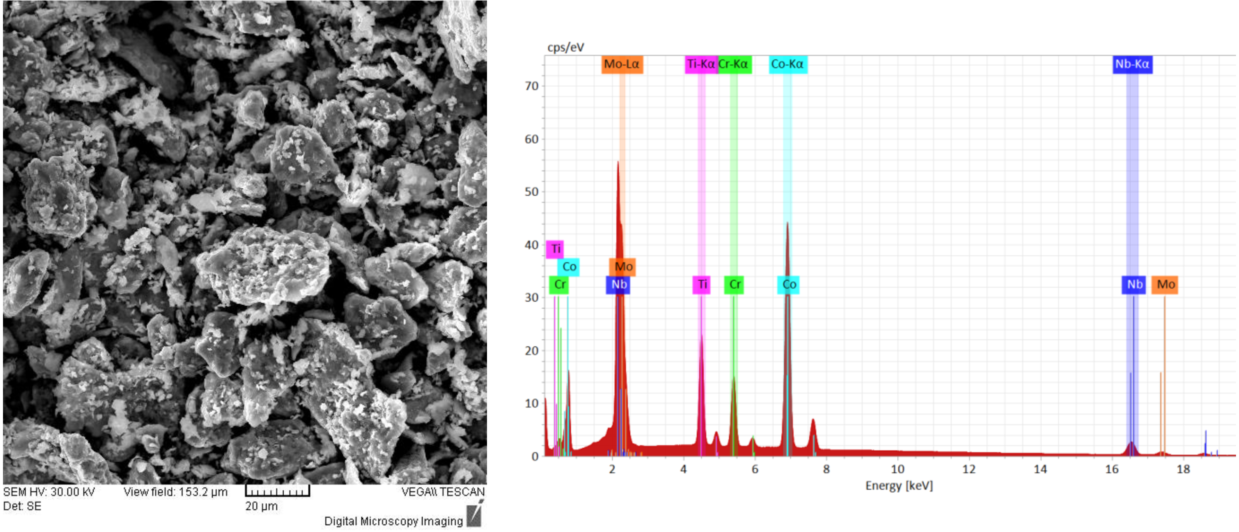


Figure 5.4. *The results of the microstructural and compositional analyzes of the HEA mixture composed of the component materials Co, Cr, Mo, Ni, Ti ground for a period of 6 h*

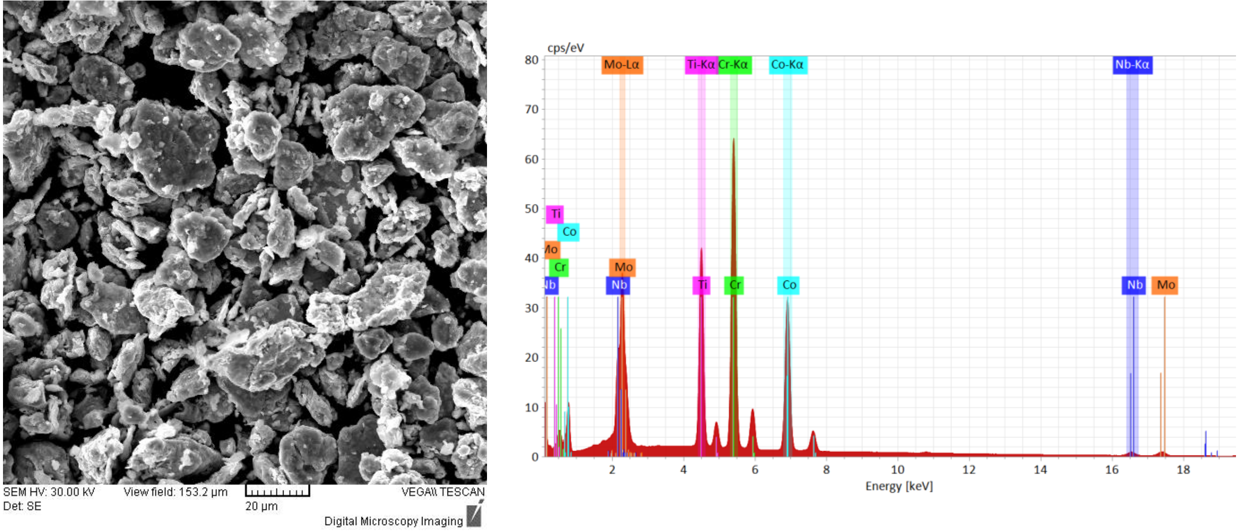


Figure 5.5*. The results of the microstructural and compositional analyzes of the HEA mixture composed of the component materials Co, Cr, Mo, Ni, Ti ground for a period of 12 h*

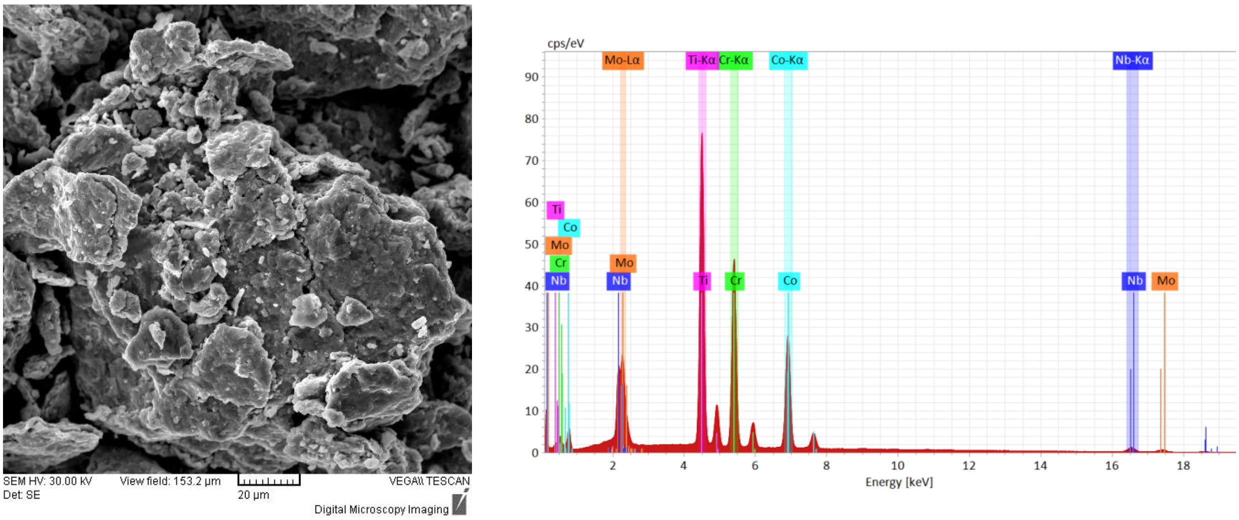


Figure 5.6. *The results of the microstructural and compositional analyzes of the HEA mixture composed of the component materials Co, Cr, Mo, Ni, Ti ground for a period of 18 h*

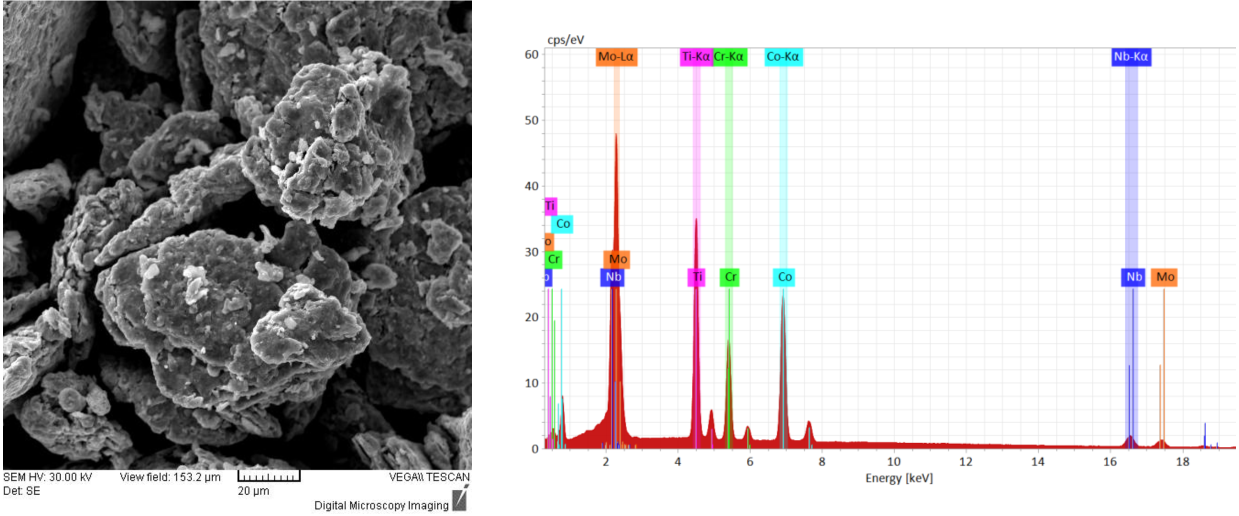


Figure 5.7*. The results of the microstructural and compositional analyzes of the HEA mixture composed of the component materials Co, Cr, Mo, Ni, Ti ground for a period of 24 h*

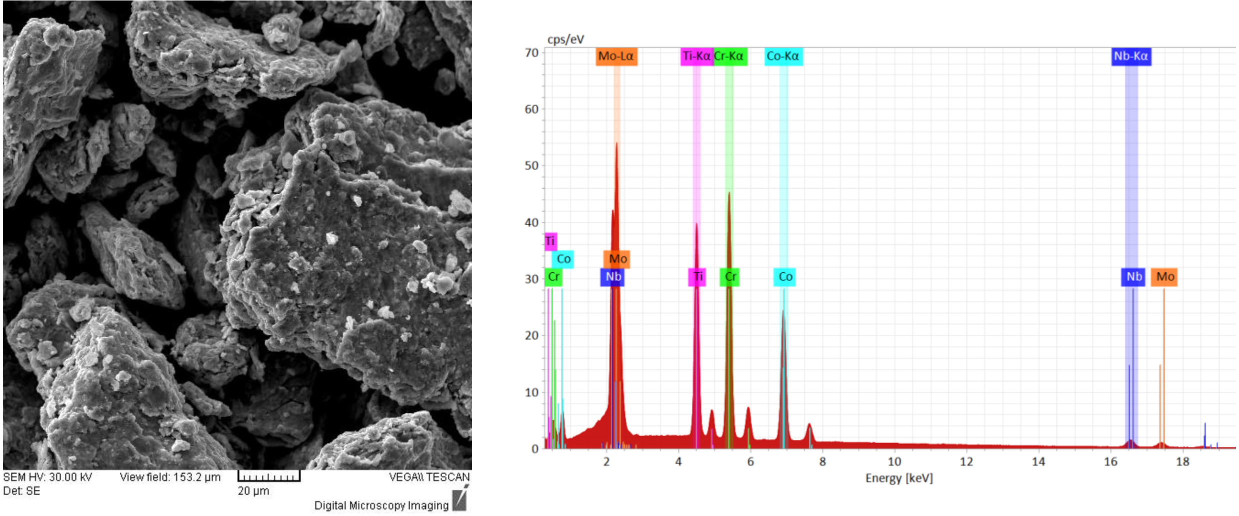


Figura 5.8. *The results of the microstructural and compositional analyzes of the HEA mixture composed of the component materials Co, Cr, Mo, Ni, Ti ground for a period of 30 h*

5.3. Technological characterization of the CoCrMoNbTi high entropy alloy powder

Caracterizarea tehnologică a aliajului cu entropie ridicată CoCrMoNbTi obţinut prin aliere mecanică, a fost realizată printr-o serie de teste prin care au fost determinate viteza de curgere, densitatea în stare vărsată şi tasată, raportul de împachetare, unghiul de taluz, dar şi dimensiunea medie de particulă. Pentru a determina influenţa alierii mecanice asupra aliajului sub formă de pulbere metalică, testările au fost realizate şi pe materialele metalice elementare sub formă de pulbere şi comparate, graficele fiind prezentate în figurile 5.11 - 5.13.

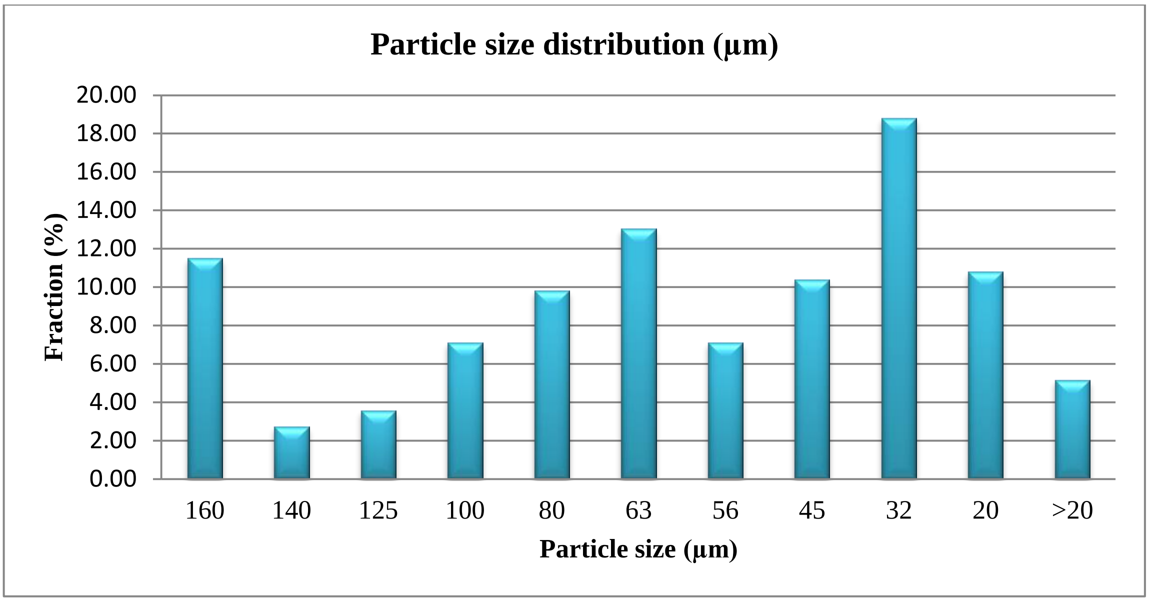


Figure 5.11. *Particle size of alloyed CoCrMoNbTi metal powders for 30 h*

Figure 5.12 shows the average particle size of the constituent elementary powders in comparison with that of the elaborated alloy. From the grain size distribution graph of the elaborated CoCrMoNbTi HEA alloy, it can be seen that the largest fraction, namely 18.82%, is represented by particles with sizes between 45 µm and 32 µm. Compared to the average size of the constituent elementary powders, a dimensional reduction of the particles of the elaborated HEA type alloy results.

Following repeated welding and fracturing processes during mechanical alloying, a fraction of 11.5% of the particles had a size greater than 160 µm, a fact that can be attributed to the Overall, the average particle size of the CoCrMoNbTi HEA alloy in powder form was determined, resulting in a value of 45.12 µm, indicating a dimensional reduction of the pure elemental metal powders of Co and Nb (figure 5.12).

In conclusion, comparing the results obtained with the average particle size of the elementary powders, a significant dimensional reduction was observed indicating the efficiency of the mechanical alloying process. The analyzed powder presents the desired composition in the present case where a high degree of alloying, mechanical alloying taking place on a nanometric scale as could be seen in figure 5.9.

Chapter 6 - Consolidation of the high entropy alloy powders in order to obtain ESD electrodes

6.1. HEA powders consolidation by Spark Plasma Sintering (SPS)

Following the mechanical alloying of the pure elemental powders in the mono-planetary ball mill and obtaining a high degree of alloying, the experiments were continued by consolidating them through the SPS sintering technique.

The sintering parameters were chosen depending on the material to be consolidated (HEA), the average melting temperature, the theoretical density of the alloy and the size of the final samples. The sintering parameters are presented in table 6.1.

Table 6.1. *Sintering parameters of BioHEA CoCrMoNbTi samples in the form of metal alloy powder*

Sample	Sintering Temp. (°C)	Force (kN)	Heating Rate (°C/min)	Cooling Rate (°C/min)	Maintaining (min)
P1	900	16	50	50	5
P2	1.000	16	50	50	5
P3	1.100	16	50	50	5

Consolidation by the SPS process is fundamentally different from conventional heating. The SPS process allows the compacts to be sintered by the Joule effect and plasma spark generated by the electric current pulsed through the compact. It is an efficient method of heating without significant losses of thermal energy. Some of the advantages of the SPS process include energy saving, rapid heating and cooling speed, reduced sintering temperature, obtaining a fine microstructure and thus improved properties.

6.2. Sintered materials characterization

The 3 samples obtained are presented in figure 6.4. The samples were then prepared metallographic in order to carry out microstructural and chemical analyzes (SEM, EDAX and Mapping) using the same equipment as in the case of powders. The same equipment was used in order to have continuity and not to influence the results through different variations.

Figure 6.4. *Macroscopic images of sintered HEA samples obtained by varying the temperature parameter*

To observe the effect of field-assisted sintering parameters on porosity and degree of densification, the compacted samples were tested by the hydrostatic method. For each sample, 5 measurements were made according to ISO 6507-1:2023 – Vickers hardness test and the average values were calculated. The results are presented in table 6.1.

Table 6.1. *Hardness measurements and hydrostatic test results for SPS sintered samples*

Sample	**Sintering Temp. (°C)**	**Average Vickers Hardness (HV)**	**Apparent Density (g/cm^3)**	**Densification Degree (%)**	**Apparent Porosity (%)**
HEA - P1	900	507,40	6,552	84,11	15,89
HEA - P2	1.000	664,37	7,394	94,91	5,08
HEA - P3	1.100	823,63	7,710	98,97	1,03

The results of the analyzes presented in table 6.1. indicates that the highest hardness was measured for the HEA - P3 sample, namely 823.63 HV, which was sintered at a temperature of 1,100°C. A high hardness implicitly indicates a higher resistance to wear, a desirable property for the case studied.

The hydrostatic density showed a degree of densification of 98.97% with an apparent density of 7.710 g/cm3 and porosity of 1.03%, indicating the best compaction among the 3 sintered samples. The results of these analyzes confirm the VEC calculation in which a potential increased hardness of the alloy was observed. In order to be able to characterize the crystallization of the alloys following compaction by sintering, XRD analyzes were carried out, and the results are presented.

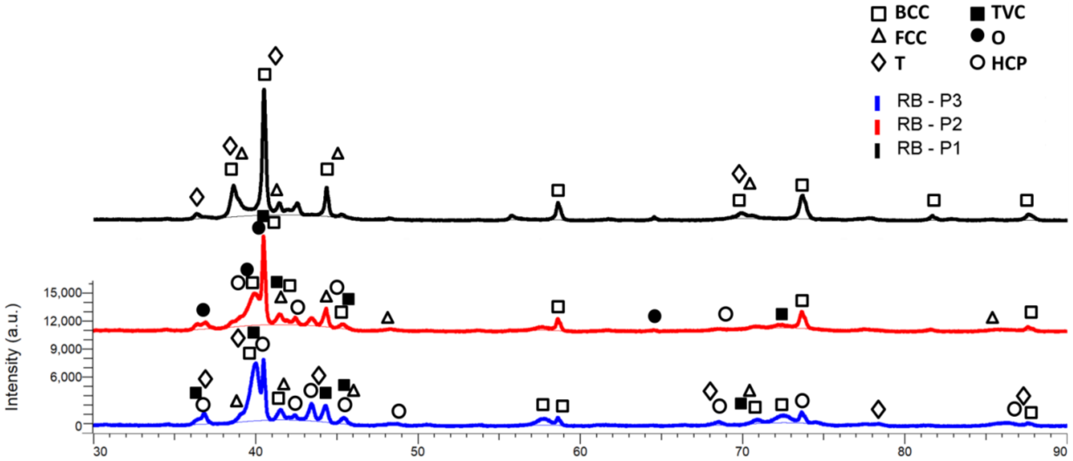


Figure 6.11. *Comparative XRD analysis for samples HEA - P1, HEA - P2 and HEA - P3*

For the sample of equiatomic CoCrFeNiTi HEA in powder form, the peak with the highest intensity was identified at the 2θ angular position of 44° with CFC and CVC as the majority phases.

Chapter 7 - Deposition of CoCrMoNbTi high entropy alloy coatings by ESD technique

7.1. Substrate preparation for high entropy alloy deposition

To make coatings with the material previously obtained by mechanical alloying and SPS sintering, metal substrates made of duplex stainless steel UNS S32750 (Super Duplex 32750) were used, which has a composition similar to that of the materials used for medical instruments in use. The chemical composition of the substrates used is presented in the following table.

Table 7.1. *Substrates chemical composition Super Duplex 32750*[2]

Constituent Element	Cr	Ni	Mo	Cu	C	Mn	N	Si	P	S	Fe
Min	24,5	6	3			0,5	0,24	0,1			Bal
Max	26	8	5	0,5	0,03	1,2	0,32	0,8	0,035	0,02	Bal

Note: Data according to the specifications given by the manufacturer Langley Alloys

The preparation of the sample surfaces in order to deposit thin layers, consists in the treatment applied to the sample surfaces with the aim of modifying them, depending on the desired type of deposit, but also cleaning them of impurities, oxides or any other types of contamination. [2.17]

By using special equipment for surface preparation, repeatability of results can be created, the main objective being to obtain a work surface as homogeneous as possible. [2.17].

Figure 7.1. *Electrode prepared for ESD deposition*

Figure 7.3 shows the stages of the deposition process, where the first sample (left) is the unprocessed cylindrical substrate, the second sample (middle) is the substrate prepared by sandblasting and cleaning with high purity alcohol (to remove residues and oxides), and the last sample (right) is the substrate coated with the developed alloy.

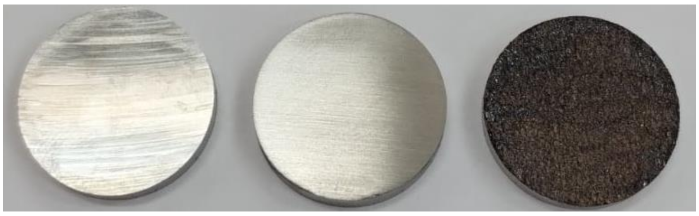
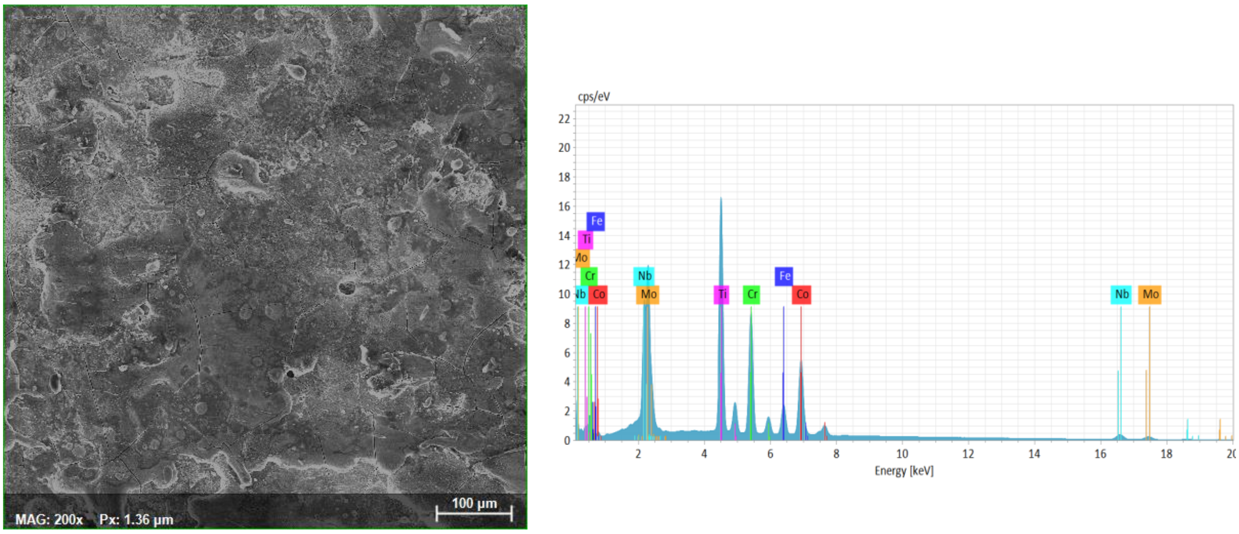


Figure. 7.3. *The stages of the actual coating with CoCrMoNbTi HEA where on the left is the raw substrate, in the middle the prepared substrate and on the right the substrate covered by the ESD technique*



Element	At.No	Net	Masic [%]	Mass Norm. [%]	Atomic [%]
Cobalt	27	5105536	16.32744	15.90257	18.61006
Chromium	24	6765611	16.49876	16.06944	21.3143
Molibdenum	42	418327	31.00788	30.201	21.71011
Niobium	41	565408	22.38545	21.80295	16.1849
Titanum	22	4960490	11.95248	11.64146	16.76848
Iron	26	1570037	4.499671	4.382582	5.412159
		Sum	100	100	100

Figure 7.4. *Results of microstructural and chemical analyzes for the coating made of CoCrMoNbTi high entropy alloy deposited by ESD.*

From the results of the mapping analysis, an increased homogeneity of the high entropy alloy deposited on the surface of the stainless steel can be observed. The elemental chemical composition is confirmed, observing a nanometric particle size for each element. It can be observed a high degree of alloying obtained following all the processes carried out and presented previously.

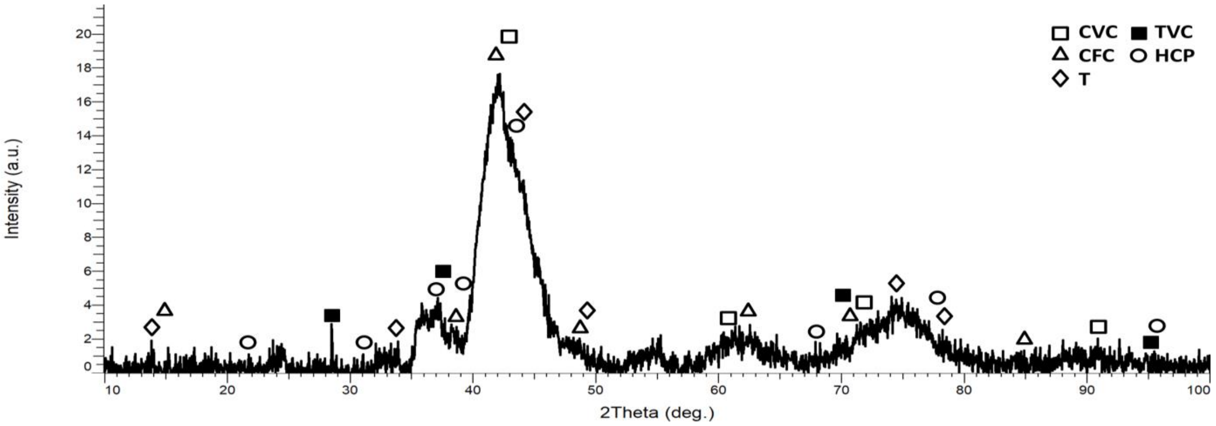


Figure 7.7. *Identification of crystallographic phases for the coating made of CoCrMoNbTi alloy with high entropy*

In addition to the mentioned majority and minority phases, a minor trigonal phase was also identified, also observed in the case of sintered samples at the 2θ angular positions of 13°, 34°, 46°, 48°, 75° and 79°.

The microalloying of the elements from the substrate in the layer is confirmed and the tendency to reduce the iron content towards the last deposition passes with CoCrMoNbTi alloy with high entropy is observed.

For testing the deposition efficiency and the influence of layer thickness (successive coating passes), an area with a significantly reduced layer fat was selected, shown in figure 7.10.

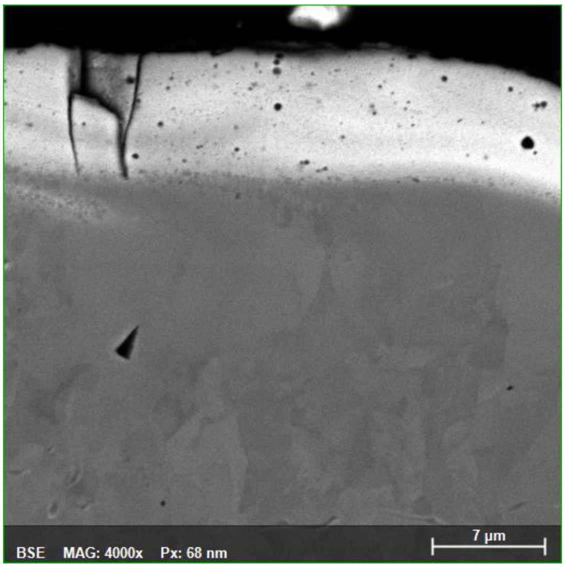


Figure 7.10 *The results of the microstructural analysis in the section with a layer thickness of about 7 µm*

Chapter 8 - Mechanical and chemical testing of the CoCrMoNbTi high entropy alloy coatings obtained by ESD technique

8.1. Corrosion resistance testing for the obtained coatings

To carry out the corrosion test, a cell was used that had in its composition a saturated calomel electrode (SCE) as a reference electrode, a platinum electrode as an auxiliary electrode and the coating or substrate as a working electrode.

The tests were performed using SBF as electrolyte at a temperature similar to the human body (37±1°C).

The Tafel curves corresponding to the tested samples are presented in Figure 8.2.

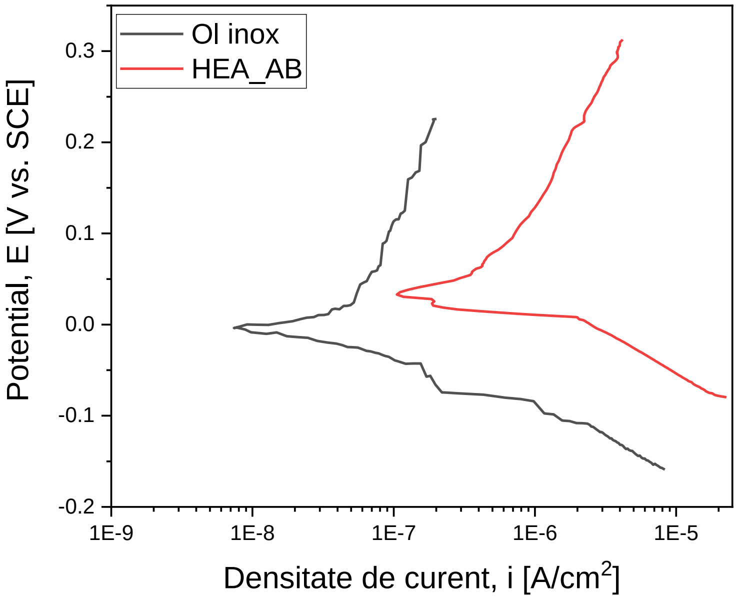


Figure 8.2. *Tafel curves corresponding to the investigated samples*

Table 8.2 presents the main electrochemical parameters used for testing.

Table 8.2. *The main electrochemical parameters*

No.	**Sample**	**E_{cor} (V)**	**i_{cor} (nA/cm^2)**	**β_c (mV)**	**β_a (mV)**	**Rp (Ωxcm^2)**	**CR (µm/year)**
1	Ol inox	-7,30	39,93	63,457	315,98	575,34	0,435
2	HEA_AB	34,84	494,81	66,876	298,526	48,01	5,341

Analyzing the electrochemical parameters from the table above, it can be said that the substrate sample (Ol stainless) presents superior electrochemical values (the lowest corrosion current density, the highest polarization resistance and the lowest corrosion rate) and thus a better corrosion behavior in SBF. Microcracks can be removed by changing deposition parameters, and corrosion tests redone to be conclusive.

8.2. Mechanical characterization of the obtained coatings (Pull-Off Testing)

The surface of the coating was prepared by mechanical cleaning with brushes and high purity alcohol to remove impurities or residues that appeared during the processes, thus ensuring a better adhesion of the adhesive used.

For this test, several variables that could affect the process were taken into account, namely:

a) the thickness of the tested layer
b) adhesive strength (between device and surface)
c) cohesive strength of the adhesive

Adhesion tests are necessary and essential in determining durability, performance, quality and more when we talk about any type of coating. This type of tests can highlight, for example, incompatibilities between the substrate and the layer, thus preventing critical failures that have a negative effect when we talk about fields such as the medical or aerospace fields.

***Figure 8.3.** Clamping rod fixed with adhesive to the tested specimen*

***Figure 8.4.** INSTRON 3380 Test Equipment*

***Figure 8.5.** Pull-Off Testing Results*

The results of both chemical and mechanical testing are relevant in the context of this doctoral thesis, taking into account that the main goal was to create solutions for the biomedical field, a very aggressive environment both from the point of view of the corrosive environment to which the instruments and implants are exposed medically, but also from the point of view of the wear that occurs during their use.

Although the adhesion results confirmed the potential of the investigated high-entropy alloy, optimization of the deposition parameters and retesting of the coating in relevant biological environments are necessary.

Chapter 9 - FINAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE DEVELOPMENT PERSPECTIVES

9.1. GENERAL CONCLUSIONS

The studies on this alloy were initially by performing thermodynamic calculations, which led to important results.

The valence electron concentration parameter indicated theoretical properties such as increased ductility and strength for the studied material. The calculated value 6 indicates the predominance of the volume-centered cubic (CVC) crystalline phase, but does not exclude the occurrence of the face-centered cubic (CFC) crystalline phase or other phases in the developed material.

It was demonstrated that the alloy meets the established criteria regarding the collective character of the constituent elements, namely the entropy and the enthalpy of mixing

The results of the microstructural and mapping analyzes show a good distribution of the elements throughout the mass and an agglomeration of the particles even at the nanometric level, which confirms that mechanical alloying has occurred.

Following the results of the XRD analyzes carried out on the metal powder, the theory was confirmed whereby the value 6 obtained for the VEC calculation indicated an abundance of CVC phases, but the value being close to the range, namely 6.8, there was the possibility of the presence of CFC phases from the tetragonal phases in areas of chromium abundance.

Metal powders were successfully compacted by electric field assisted sintering (SPS) technique with varying temperature parameter

The results showed that for the sintering temperature of 1100°C a degree of densification of 98.97% and porosity of 1.03% was obtained, indicating the best compaction among the 3 sintered samples. The apparent density determined was 7,710 g/cm3.

The coatings were obtained by applying to a super duplex stainless steel substrate through the successive application of several layers.

The presence of iron in a mass amount of approximately 5% was observed on the surface, indicating the effect of microalloying following the electrical spark deposition process.

From the results of the EDS profile line analysis of the cross-section of the sample coated with CoCrMoNbTi alloy with high entropy, it can be seen how the iron content decreases with the increase in the thickness of the deposited layer

After the depositions, the coatings were chemically tested by corrosion testing in a relevant biomedical environment, respectively SBF and mechanically tested by pull-off test.

Corrosion results were not favorable for the coating compared to the stainless steel substrate, although there are no significant differences. It was considered that there were transverse microcracks that could influence the testing of the material

From the results of the pull-off test, the coated sample presented an increased adhesion strength, with no visible adhesive or cohesive breaks in the material, thus indicating the efficiency of electrical spark deposition.

9.2. ORIGINAL CONTRIBUTIONS

The original contributions of this PhD thesis are mainly driven by the novelty of the topic of high entropy alloys for the biomedical field, whether used as coatings or compact samples.

First of all, the novelty is brought by the thermodynamic study carried out for the investigated high-entropy alloy CoCrMoNbTi.

I managed to determine the optimal solid state processing parameters of pure metal powders to obtain the high entropy alloy CoCrMoNbTi with a high degree of alloying and homogeneity.

I studied the evolution of the degree of alloying at well-established time intervals, observing the progress during the process.

I determined the pressing curve during sintering assisted in an electric field for the CoCrMoNbTi alloy, because no technical data published in the specialized literature regarding the processing parameters for the studied alloy were identified, the sintering parameters being determined after performing preliminary tests until obtaining a satisfactory result.

Another element of novelty was obtaining electrodes for deposition from CoCrMoNbTi alloy with high entropy, this being an element of total novelty.

We obtained a homogeneous coating with good adhesion that can be successfully used in biomedical applications where high wear resistance is required.

Finally, we tested the high entropy alloy in the form of coatings in the relevant environment, namely SBF, there being no literature references for this subject, observing the effects produced during testing.

9.3. FUTURE DEVELOPMENT PERSPECTIVES

Further development prospects include improving the deposition process to obtain layers without microcracks considering the fact that this is a manual process at high temperatures.

Modification of the deposition parameters are required in order to avoid contamination with materials from the substrate or the use of a biocompatible intermediate layer.

Carrying out corrosion tests in the relevant environment (SBF) on the material in compact form, namely on the sintered samples assisted in an electric field.

Carrying out tribological tests is necessary on the covered surfaces.

Scratch testing on coatings to check safety, performance and durability.

In addition to those mentioned, additional adhesion tests are required to identify the point where adhesive and/or cohesive breaks will occur, thus indicating the field of applicability.

I also want to disseminate the results regarding the results obtained after obtaining coatings in international conferences (RoMat2024, Bucharest, Romania, 2024) and ISI or BDI indexed journals (Materials, Coatings, Applied Sciences).

REFERENCES

PART I - THEORETICAL STUDY OF ALLOYS WITH COMPLEX COMPOSITION FOR AGGRESSIVE ENVIRONMENTS WITH POTENTIAL BIOMEDICAL APPLICATIONS

[1.1] Yeh, J.W.; Chen, S.K.; Lin, S.J.; Gan, J.Y.; Chin, T.S.; Shun, T.T.; Tsau, C.H.; Chang, S.Y. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303.

[1.2] Cantor, B.; Chang, I.; Knight, P.; Vincent, A. Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* **2004**, *375–377*, 213–218.

[1.3] Sunil Munakomi, A pilot study comparing pattern of damage sustained among instruments from different surgical units in a tertiary care centre in Nepal – reappraising the role of instrument reprocessing in retaining their value, F1000Research, 2018, vol. 7, 102

[1.4] Weihong Jin, Paul K. Chu, Orthopedic Implants, Reference Module in Biomedical Sciences Encyclopedia of Biomedical Engineering 2019, Pages 425-439

[1.5] Eliaz N. Corrosion of metallic biomaterials: a review. Materials 2019;12:407. https://doi.org/10.3390/ma12030407.

[1.6] Liu P, Lu FF, Liu GJ, Mu XH, Sun YG, Zhang QD, et al. Roboticassisted unicompartmental knee arthroplasty: a review. Arthroplasty 2021;3:15. https://doi.org/10.1186/s42836-021- 00071-x.

[1.7] Ali S, Rani AMA, Baig Z, Ahmed SW, Hussain G, Subramaniam K, et al. Biocompatibility and corrosion resistance of metallic biomaterials. Corrosion Rev 2020;38:381e402. https://doi.org/10.1515/corrrev-2020-0001.

[1.8] Kumar P, Jain NK. Finite element analysis of femoral prosthesis using Ti-6Al-4V alloy and TiNbZrTaFe high entropy alloy. Mater Today Proc 2021;44:1195e201. https:// doi.org/10.1016/j.matpr.2020.11.239.

[1.9] Bairagi D, Mandal S. A comprehensive review on biocompatible Mg-based alloys as temporary orthopedic implants: current status, challenges, and future prospects. J Magnes Alloys 2022;10:627e69. https://doi.org/10.1016/ j.jma.2021.09.005.

[1.10] Ryu DJ, Jung A, Ban HY, Kwak TY, Shin EJ, Gweon B, et al. Enhanced osseointegration through direct energy deposition porous coating for cementless orthopedic implant fixation. Nature: Sci Rep 2021;11:22317. https://doi.org/10.1038/ s41598-021-01739-9.

[1.11] Li Y, Yang C, Zhao H, Qu S, Li X, Li Y. New developments of Ti-based alloys for biomedical applications. Materials 2014; 7: 1709e800. https://doi.org/10.3390/ma7031709.

[1.12] Baron S, Desmond D, Ahearne E. The fundamental mechanisms of wear of cemented carbide in continuous cutting of medical grade cobalt chromium alloy (ASTM F75). Wear 2019;424e425:89e96. https://doi.org/10.1016/ j.wear.2019.01.096.

[1.13] Zhang XY, Fang G, Leeflang S, Zadpoor AA, Zhou J. Topological design, permeability and mechanical behavior of additively manufactured functionally graded porous metallic biomaterials. Acta Biomater 2019;84:437e52. https://doi.org/ 10.1016/j.actbio.2018.12.013.

[1.14] Fikeni L, Annan KA, Seerane M, Mutombo K, Machaka R. Development of a biocompatible Ti-Nb alloy for orthopaedic Applications. IOP Conf Ser Mater Sci Eng 2019;655:012022. https://doi.org/10.1088/1757-899X/655/1/012022.

[1.12] Grimalt MAL, Genestra MAF, Rodriguez VA, Ramis JM, Monjo M. Nanostructured titanium for improved endothelial biocompatibility and reduced platelet adhesion in stent applications. Coatings 2020;10:907. https://doi.org/10.3390/coatings10090907.

[1.15] Sarraf M, Ghomi ER, Alipour S, Ramakrishna S, Sukiman NL. A state-of-the-art review of the fabrication and characteristics of titanium and its alloys for biomedical applications. Bio-Design Manuf 2022;5:371e95. https://doi.org/10.1007/s42242-021-00170-3.

[1.16] Campanelli LC. A review on the recent advances concerning the fatigue performance of titanium alloys for orthopedic applications. J Mater Res 2021;36:151e65. https://doi.org/ 10.1557/s43578-020-00087-0.

[1.17] Sola A, Nouri A. Microstructural porosity in additive manufacturing: the formation and detection of pores in metal parts fabricated by powder bed fusion. J Adv Manuf Process 2019;1:1e21. https://doi.org/10.1002/amp2.10021.

[1.18] Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang, High-entropy alloy: challenges and prospects, Materials Today, Vol. 19, Issue 6, 2016.

[1.19] J.W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, S.-Y. Chang, Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes, Advanced Engineering Materials, Vol. 6, Issue 5, pp. 299-303

[1.20] B. Cantor, I. T. H. Chang, P. Knight, A. J. B.Vincent, Microstructural development in equiatomic multicomponent alloys, Materials Science and Engineering: A, Vol. 375–377, 2004, pp. 213-218

[1.21] Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang, Design of high entropy alloys: A single-parameter thermodynamic rule, Scripta Materialia, Vol. 104, 2015, pp. 53-55

[1.22] Y. Zhang, Microstructures and properties of high entropy alloys, Progress in Material Science, Vol. 61, 2014, pp. 1-93.

[1.23] B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, R. O. Ritchie, A fracture-resistant high-entropy alloy for cryogenic applications, Science, Vol. 345, Issue 6201, 2014, pp. 1153-1158.

[1.24] M.A. Hemphill, et al. Acta Mater. 60 (16) (2012) 5723. M. A. Hemphill, T. Yuan, G. Y. Wang, J. W. Yeh, C. W. Tsai, A. Chuang, P. K. Liaw, Fatigue behavior of Al0.5CoCrCuFeNi high entropy alloys, Acta Materialia, Vol. 60, Issue 16, 2012, pp. 5723-5734.

[1.25] K.H. Huang, J.W. Yeh, A study on multicomponent alloy systems containing equal-mole elements. Hsinchu: National Tsing Hua University, 1996.

[1.26] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, Adv Eng Mater, Vol. 6, 2004, pp. 299–303.

[1.27] J.W. Yeh, Recent progress in high-entropy alloys, Ann Chim-Sci Mat.,Vol. 31, 2006, pp. 633–648.

[1.28] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in Equiatomic Multicomponent Alloys, Mat. Sci. Eng. A375 (2004) 213-218

[1.29] Z. Li, S. Zhao, R. O. Ritchie, M. A. Meyers, Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys, Progress in Materials Science, Vol. 102, 2019, pp. 296–345

[1.30] K.H. Cheng, C.H. Lai, S.J. Lin, J.W. Yeh, Recent progress in multi-element alloy and nitride coatings sputtered from high-entropy alloy targets, Ann Chim-Sci Mat, Vol. 31, 2006, pp. 723–736.

[1.31] I.S. Aristeidakis, M.I.T. Tzini, High Entropy Alloys, 2016, pp. 5-40.

[1.32] Nova K, Nov ak P, Dvorsky ´ D. Influence of alloying elements on the mechanical properties of a cobalt-based alloy produced with powder metallurgy. Mater Technol 2017;51:443e7. https://doi.org/10.17222/mit.2016.054.

[1.33] Ingarao G, Priarone PC. A comparative assessment of energy demand and life cycle costs for additive- and subtractivebased manufacturing approaches. J Manuf Process 2020;56:1219e29. https://doi.org/10.1016/ j.jmapro.2020.06.009.

[1.34] Cheng Z, Li Y, Xu C, Liu Y, Ghafoor S, Li F. Incremental sheet forming towards biomedical implants: a review. J Mater Res Technol 2020;9:7225e51. https://doi.org/10.1016/ j.jmrt.2020.04.096.

[1.35] Kim HG, Kim WR, Park HW, Bang GB, Jung KH, Son Y, et al. Microstructural study of the nano-scale martensitic lamellar a-Co and ε-Co phases of a CoeCr alloy fabricated by selective laser melting. J Mater Res Technol 2021;12:437e43. https:// doi.org/10.1016/j.jmrt.2021.03.006.

[1.36] Almanza E, Perez MJ, Rodrı ´guez NA, Murr LE. Corrosion resistance of Ti-6Al-4V and ASTM F75 alloys processed by electron beam melting. J Mater Res Technol 2017;6:251e7. https://doi.org/10.1016/j.jmrt.2017.05.003.

[1.37] Kajima Y, Takaichi A, Kittikundecha N, That HL, Cho HHW, Tsutsumi Y, et al. Reduction in anisotropic response of corrosion properties of selective laser melted Co-Cr-Mo alloys by post-heat treatment. Dent Mater 2021;37:e98e108. https://doi.org/10.1016/j.dental.2020.10.020.

[1.38] Xiang S, Yuan Y, Zhang C, Chen J. Effects of process parameters on the corrosion resistance and biocompatibility of Ti-6Al-4V parts fabricated by selective laser melting. ACS Omega 2022;7:5954e61. https://doi.org/10.1021/acsomega.1c06246.

[1.39] Lyons R, Newell A, Ghadimi P, Papakostas N. Environmental impacts of conventional and additive manufacturing for the production of Ti-6Al-4V knee implant: a life cycle approach. Int J Adv Manuf Technol 2021;112:787e801. https://doi.org/ 10.1007/s00170-020-06367-7

[1.40] A. Li, D. Ma, and Q. Zheng, Effect of Cr on Microstructure and Properties of a Series of AlTiCrxFeCoNiCu High-Entropy Alloys, J. Mater. Eng. Perform., 2014, 23, p 1197–1203

[1.41] C. Sajith Babu, K. Sivaprasad, V. Muthupandi, and J.A. Szpunar, Characterization of Nanocrystalline AlCoCrNiFeZn high entropy alloy produced by mechanical alloying, Proc. Mater. Sci., 2014, 5, p 1020–1026

[1.42] B. Zhang, M.C. Gao, Y. Zhang, S. Yang, and S.M. Guo, Senary refractory high entropy alloy MoNbTaTiVW, Mater. Sci. Technol., 2015, 31, p 1207–1213

[1.43] H. Jiang, L. Jiang, K. Han, L. Yiping, T. Wang, Z. Cao, and T. Li, Effects of Tungsten on Microstructure and Mechanical Properties of CrFeNiV0.5Wx and CrFeNi2V0.5Wx High-Entropy Alloys, J. Mater. Eng. Perform., 2015, 24, p 4594–4600

[1.44] N.N. Guo, L. Wang, L.S. Luo, X.Z. Li, R.R. Chen, Y.Q. Su, J.J. Guo, and H.Z. Fu, Microstructure and Mechanical Properties of Refractory High Entropy (Mo0.5NbHf0.5ZrTi)BCC/M5Si3 In-Situ Compound, J. Alloy. Compd., 2016, 660, p 197–203

[1.45] Zhang, M., Zhou, X. & Li, J. Microstructure and Mechanical Properties of a Refractory CoCrMoNbTi High-Entropy Alloy. J. of Materi Eng and Perform 26, 3657–3665 (2017). https://doi.org/10.1007/s11665-017-2799-z

[1.46] N.N. Guo, L. Wang, L.S. Luo, X.Z. Li, R.R. Chen, Y.Q. Su, J.J. Guo, and H.Z. Fu, Microstructure and Mechanical Properties of In-Situ MCCarbide Particulates-Reinforced Refractory High-Entropy Mo0.5NbHf0.5ZrTi Matrix Alloy Composite, Intermetallics, 2016, 69, p 74–77

[1.47] O.N. Senkov, G.B. Wilks, D.B. Miracle, C.P. Chuang, and P.K. Liaw, Refractory High-Entropy Alloys, Intermetallics, 2010, 18, p 1758– 1765

[1.48] O.N. Senkov, J.M. Scott, S.V. Senkova, F. Meisenkothen, D.B. Miracle, and C.F. Woodward, Microstructure and Elevated Temperature Properties of a Refractory TaNbHfZrTi Alloy, J. Mater. Sci., 2012, 47, p 4062–4074

[1.49] HE Longjun, ZHANG Mina, YE Xuyang, RUAN Dianbo, ZHANG Wenwu, CoCrMoNbTi refractory high-entropy alloys prepared by mechanical alloying combined with laser cladding, Powder Metallurgy Technology, 2023, 41(6): 500-507, DOI: 10.19591/j.cnki.cn11-1974/tf.2021080011

[1.50] Peng H Y, Kang Z X, Li X Z, et al., Effects of milling time on the microstructure and properties of NbMoTaWVCr refractory high entropy alloy, Powder Metall Mater Sci Eng, 2020, 25(6): 513

[1.51] Xianglin Zhou, Longjun He, Mina Zhang, Peng Wang, Effect of ceramic particles on microstructure and properties of CoCrMoNbTi high-entropy alloy coating fabricated by laser cladding, Optik, Volume 285, 2023, 170987, https://doi.org/10.1016/j.ijleo.2023.170987.

[1.52] Q. An, J. Wang, Y. Liu, B. Liu, W. Guo, Q. Fang, Y. Nie, Effects of C and Mo on microstructures and mechanical properties of dual-phase high entropy alloys, Intermetallics (2019) 110.

[1.53] G. Lian, J. Zeng, C. Chen, X. Huang, Performance and efficiency control method of in-situ TiC generated by laser cladding, Optik 220 (2020), 165221.

[1.54] C. Suryanarayana, Mechanical alloying and milling, Progress in Materials Science, Vol. 46 2001, pp. 1-184

[1.55] C. Suryanarayana, Mechanical milling/alloying of intermetallics, Intermetallics, Vol. 4, Issue 5, 1996, pp. 339-355

[1.56] C. Suryanarayana, Mechanical alloying and milling, Marcel Dekker, 2004

[1.57] G. M. Chow, N. I. Noskova, Nanostructured Materials, Science and Technology, Vol. 50, 2012.

[1.58] L.M. Di, H. Bakker, Phase transformation of the compound V3Ga induced by mechanical grinding, Journal of Physics: Condenssed Matterials, Vol. 3, 1991, pp. 3427–3432.

[1.59] C. Suryanarayana, E. Ivanov, R. Noufi, M.A. Contreras, J.J. Moore, Phase Selection in a Mechanically Alloyed Cu-In-Ga-Se Powder Mixture, Journal of Materials Research, Vol. 14, 1999, pp. 377–383.

[1.60] B.L. Chu, C.C. Chen, T.P. Perng, Amorphization of Ti1−x Mn x, Metallurgical Transactions A, Vol. 23, 1992, pp. 2105–2110.

[1.61] K. Tokumitsu, Synthesis of Metastable Fe3C, Co3C and Ni3C by Mechanical Alloying Method, Material Science Forum , Vol. 235, 1997, pp. 127–132.

[1.62] B.K. Yen, T. Aizawa, J. Kihara, Synthesis and formation mechanisms of molybdenum silicides by mechanical alloying, Material Science Engineering, Vol. 220, 1996, pp. 8–14.

[1.63] B.K. Yen, T. Aizawa, J. Kihara, Reaction synthesis of refractory disilicides by mechanical alloying and shock reactive synthesis techniques, Materials Science and Engineering. A, Vol. 240, 1997, pp. 515-521.

[1.64] M. Sherif El-Eskandarany, Solid state nitrization reaction of amorphous tantalum aluminium nitride alloy powders: the role of amorphization by reactive ball milling, Journal of Alloys and Compounds, Vol. 203, 1994, pp. 117–126.

[1.65] El-Eskandarany, M.S., Zhang, W. & Inoue, A. Mechanically induced solid-state reaction for synthesizing glassy Co75Ti25 soft magnet alloy powders with a wide supercooled liquid region. Journal of Materials Research, Vol. 17, 2002, pp. 2447–2456.

[1.66] A. Tonejc, D. Duzevic, A. M. Tonejc, Estimation of peak temperature reached by particles trapped among colliding balls in the ball-milling process using excessive oxidation of antimony, Scripta Metallurgica et Materialia, Vol. 25, 1991, pp. 1111-1113.

[1.67] T. Ohtani, K. Maruyama, K. Ohshima, Synthesis of copper, silver, and samarium chalcogenides by mechanical alloying, Materials Research Bulletin, Vol. 32, 1997, pp. 343–350.

[1.68] M. Sherif El-Eskandarany, Synthesis of nanocrystalline titanium carbide alloy powders by mechanical solid state reaction, Metallurgical and Materials Transactions A, Vol. 27A, 1996, pp. 2374–2382.

[1.69] O. Abe, Y. Suzuki, Mechanochemically preparation of BT powders, Materails Science Forum, Vol. 225, 1996, pp. 563–568.

[1.70] T. Fukunaga, K. Nakamura, K. Suzuki, U. Mizutani, Amorphization of PVA powders by mechanical milling, Journal of the Japan Society of Powder and Powder Metallurgy, Vol. 43, 1996, pp. 726-730.

[1.71] T. Fukunaga, K. Nakamura, K. Suzuki, U. Mizutani, Amorphization of PVA powders by mechanical milling, Journal of the Japan Society of Powder and Powder Metallurgy, Vol. 43, 1996, pp. 726-730.

[1.72] T. Fukunaga, M. Mori, K. Inou, U. Mizutani, Amorphization in an immiscible Cu-V system by mechanical alloying and its structure observed by neutron diffraction, Material Science Engineering, Vol. 134, 1991, pp. 863–866.

[1.73] C.H. Lee, T. Fukunaga, U. Mizutani, Temperature dependence of mechanical alloying and grinding in Ni-Zr, Cu-Ta and Fe-B alloy systems, Material Science Engineering, Vol. 134, 1991, pp. 1334–1337.

[1.74] C.H. Lee, M. Mori, T. Fukunaga, K. Sakurai, U. Mizutani, Effect of mechanically alloying beyond the completion of glass formation for Ni-Zr alloy powders, Material Science Forum, Vol. 88, 1992, pp. 399–406.

[1.75] L. Lu, M.O. Lai, The Mechanical Alloying Process, Mechanical Alloying. Boston, MA: Kluwer, 1998, pp. 23-67.

[1.76] H.U. Kessel, J. Hennicke, J. Schmidt, T. Weiβgärber, B.F. Kieback, M. Herrmann, J. Räthel, “FAST” field assisted sintering technology – a new process for the production of metallic and ceramic sintering materials, FCT Systeme GmbH, 2010, p. 1-37, http://www.fct-systeme.de/dynamic/dlFile/300c4826460727695d31a2f6ff104235.dl/20091127111759_Plansee05-2009_EN.pdf

[1.77] H.U. Kessel, J. Hennicke, R. Kirchner, T. Kessel, Rapid sintering of novel materials by FAST/SPS – Further development to the point of an industrial production process with high cost efficiency, FCT Systeme GmbH, 2010, 96528, http://www.fct-systeme.de/download/20100225123420/FCT-Sintered-Materials.pdf

[1.78] O. Guillon, J. Gonzalez-Julian, B. Dargatz, T. Kessel, G. Schierning, J. Räthel, M. Herrmann, Field-assisted sintering technology / spark plasma sintering: mechanisms, materials, and technology developments, Advanced Engineering Materials, 2014, Vol. 16, Issue 7, p. 830-849.

[1.79] Y. Liu, J. Wang, Q. Fang, B. Liu, Y. Wu, and S. Chen, Preparation of superfine-grained high entropy alloy by spark plasma sintering gas atomized powder, Intermetallics, Vol. 68, 2016, pp. 16-22.

[1.80] Laura Elena Geambazu, Ciprian Alexandru Manea, Ioana Csaki, Depunerea de straturi subțiri. Îndrumar de laborator, Universitatea Politehnica Bucuresti ISBN: 978-606-25-0785-5, 2023

[1.81] C. L. Jenney, A. O’Brien, Welding Handbook, Vol. 3, 9th ed., 2007 pp. 598 – 602.

[1.82] R. N. Johnson, G. L. Sheldon, Advances in the electro spark deposition coating process. Journal of Vacuum Science & Technology A, Vol. 4, Issue 6, 1986, pp. 2740 – 2746

[1.83] S. K. Tang, The Process Fundamentals and Parameters of Electro-Spark Deposition, A thesis presented to the University of Waterloo in fulfillment of the thesis requirement for the degree of Master of Applied Science in Mechanical Engineering, 2009

[1.84] TechnoCoat, SparkDepo Elecrospark Coating and Overlay Operating Manual, Model 200/300/500, Ver. 3-5, 2015

[1.85] J. L. Reynolds, R. L. Holdren, L. E. Brown., Electro-Spark Deposition, Advanced Materials and Process, Vol. 161, Issue 3, 2003

[1.86] R.N. Johnson, ElectroSpark Deposition: Principles and Applications, 45th Annual Technical Conference Proceedings, 2002, pp.87 – 92

[1.87] I. V. Galinov, R. B. Luban, Mass Transfer Trends during Electro-spark Alloy, Surface Coating Technology, Vol.79, 1996, pp. 9-18

[1.88] P.Z. Wang, G.S. Pan, Y. Zhou, J.X. Qu, and H.S. Shao, Accelerated Electrospark Deposition and the Wear Behavior of Coatings, Journal of Materials Engineering and Performance, Vol. 1997, pp. 780-784.

PART II - STUDIES AND PERSONAL EXPERIMENTAL RESEARCH

[2.1] A.R. Miedema, F.R. de Boer, and R. Boom, CALPHAD, Vol. 1, 1977.

[2.2] S. Guo, C. T. Liu, Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase, Progress in Natural Science: Materials International, Vol. 21, 2011, pp. 433−446

[2.3] Y. Zhang, Y. J. Zhou, J. P. Lin, Solid-solution phase formation rules for multi-component alloys, Advanced Engineering Materials, Vol. 10, 2008, pp. 534−538.

[2.4] J. W. Yeh, S. K. Chen, S. J. Lin, Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes, Advanced Engineering Materials, Vol. 6, 2004, pp. 299−303.

[2.5] B. Cantor, I. T. H. Chang, P. Knight, Microstructural development in equiatomic multicomponent alloys, Materials Science and Engineering A,, Vol. 375−377, 2004, pp. 213−218.

[2.6] W. H. Wu, C. C. Yang, J. W. Yeh, Industrial development of high-entropy alloys, Annales De Chimie-Science Des Materiaux, Vol. 31, 2006, pp.737−747.

[2.7] J. W. Yeh, Recent progress in high-entropy alloys, Annales De Chimie-Science Des Materiaux, Vol. 31, 2006, pp. 633−648.

[2.8] Manea, C.A.; Geambazu,L.E.; T˘alpeanu, D.; Marinescu, V.;Sbârcea, G.B.; P˘atroi, D.; Udrea, R.M.;Lungu, M.V.; Lucaci, M. CoxCrFeNiTi High-Entropy Alloys Prepared via Mechanical Alloying and Spark Plasma Sintering for Magnetron Sputtering Coatings. Materials 2023, 16, 6386. https://doi.org/10.3390/ma16196386

[2.9] Peters, M.; Hemptenmacher, J.; Kumpfert, J.; Leyens, C. Structure and properties of titanium and titanium alloys. In Titanium and Titanium Alloys; Leyens, C., Peters, M., Eds.;Wiley-VCH Verlag GmbH & Co. KGaA:Weinheim, Germany, 2005; pp. 1–36.

[2.10] Rogal, L.; Ikedab, Y.; Lai, M.; Körmannb, F.; Kalinowska, A.; Grabowski, B. Design of a dual-phase hcp-bcc high entropy alloy strengthened by ω nanoprecipitates in the Sc-Ti-Zr-Hf-Re system. Mater. Des. 2020, 192, 108716

[2.11] Chung, D.; Kwon, H.; Eze, C.; Kim,W.; Na, Y. Influence of Ti Addition on the Strengthening and Toughening Effect in CoCrFeNiTix Multi Principal Element Alloys. Metals 2021, 11, 1511. [CrossRef]

[2.12] Bololoi, A.E.; Geambazu, L.E.; Antoniac, I.V.; Bololoi, R.V.; Manea, C.A.; Cojocaru, V.D.; Pătroi, D. Solid-State Processing of CoCrMoNbTi High-Entropy Alloy for Biomedical Applications. Materials 2023, 16, 6520. https://doi.org/10.3390/ma16196520

[2.13] C.J. Boehlert Part III. The tensile behavior of Ti-Al-Nb O Bcc orthorhombic alloys Metall. Mater. Trans. A., 32 (2001), pp. 1977-1988

[2.14] N. Yurchenko, E. Panina, M. Tikhonovsky, G. Salishchev, S. Zherebtsov, N. Stepanov, A new refractory Ti-Nb-Hf-Al high entropy alloy strengthened by orthorhombic phase particles, International Journal of Refractory Metals and Hard Materials, vol. 92, 2020, 105322, ISSN 0263-4368

[2.15] T. Zhang, R.D. Zhao, F.F. Wu, S.B. Lin, S.S. Jiang, Y.J. Huang, S.H. Chen, J. Eckert, Transformation-enhanced strength and ductility in a FeCoCrNiMn dual phase high-entropy alloy, Materials Science and Engineering: A, Volume 780, 2020, 139182, ISSN 0921-5093, https://doi.org/10.1016/j.msea.2020.139182.

[2.16] Guo, S.; Liu, C.T. Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase. Prog. Nat. Sci. Mater. Int. 2011, 21, 433−446.

[2.17] L. E. Geambazu, C. A. Manea, I. Csàki, Depunerea de straturi subţiri – Îndrumar de laborator, Editura MatrixRom, ISBN , 978-606-25-0785-5, 2023, 118 pag.

[2.18] Carter, C. Barry, and M. Grant Norton. Ceramic Materials: Science and Engineering. Springer, 2007. ISBN: 978-0387462707.

[2.19] Engineered Materials Handbook, Volume 4: Ceramics and Glasses. ASM International, 1991. ISBN: 978-0871702823.

RESULTS DISSEMINATION

The results of this PhD thesis entitled **"Studies and research on coatings obtained from high entropy alloys produced by solid state processing for biomedical applications"** were disseminated in **3 ISI rated articles**, of which 2 with an impact factor of 3.1 from Q1 and 1 article with an impact factor of 0.3 (of which 2 articles are as the main author), but also through 2 presentations at national and international scientific events:

ARTICLES INDEXED ISI IN THE DOCTORAL THESIS FIELD

1. **Bololoi A.E.**, Geambazu L.E., Antoniac I.V., Bololoi R.V., Manea C.A., Cojocaru V.D., Pătroi D., **The Influence Of Spark Plasma Sintering Parameters On The Physical Properties Of CoCrMoNbTi Bio-HEA**, University Politehnica Of Bucharest Scientific Bulletin Series B-Chemistry And Materials Science, Volume: 83, Issue: 1, Pages: 165-174, 2024, ISSN 1454-2331, **IF=0,3**

2. **Bololoi A.E.**, Geambazu L.E., Antoniac I.V., Bololoi R.V., Manea C.A., Cojocaru V.D., Pătroi D., **Solid-State Processing of CoCrMoNbTi High-Entropy Alloy for Biomedical Applications,** Materials 2023, 16, 6520, DOI10.3390/ma16196520, WOS:001089169100001, PubMed ID 37834657, eISSN 1996-1944 **IF=3.1**

3. Geambazu LE, Tălpeanu D., Bololoi RV, Manea CA, **Bololoi AE**, Miculescu F, Pătroi D, Cojocaru VD, ***Microstructural Characterization of Al0.5CrFeNiTi High Entropy Alloy Produced by Powder Metallurgy Route***, Materials, 16, 2023, 7038, DOI10.3390/ma16217038, WOS:001103322100001, PubMed ID 37959635, eISSN, 1996-1944 **IF=3.1**

DISSEMINATIONS WITHIN NATIONAL AND INTERNATIONAL SCIENTIFIC EXHIBITIONS

1. **Alina Elena Bololoi**, Laura Elena Geambazu, Iulian Vasile Antoniac, Robert Viorel Bololoi, Ciprian Alexandru Manea, Dănuț Vasile Cojocaru, Delia Pătroi, **Solid State Processing of CoCrMoNbTi High Entropy Alloy for Biomedical Applications**, BioReMed2023, 19-21 Iulie 2023, Sibiu, Romania

2. Laura Elena Geambazu, **Alina Elena Bololoi***, Iulian Vasile Antoniac, Robert Viorel Bololoi, Ciprian Alexandru Manea, Vasile Dănuţ Cojocaru And Delia Pătroi, **Multicomponent Complex Alloys For Biomedical Aplications Produced By Powder Metallurgy**, Asmes 2024, 9-12 Mai 2024, Tulcea, Romania