

**NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
“IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE”**

**E.O. Paton Institute of Materials Science and Welding
Department of High Temperature Materials and Powder Metallurgy**

«On the rights of the manuscript»
УДК 621.793.79

«Admission to the defence»
Head of the department
_____ I.I. Bogomol
«__» _____ 2021

**Master's thesis
for a master's degree
in the specialty 132 Materials Science
on the topic: «Structure and mechanical properties of multicomponent
AlNiCoFeCrTiMo alloy obtained by mechanical alloying and sintering»**

Performed by
second-year student of group FN-01mp
Shao Yiru _____

Research supervisor:

professor of the department of HTM and PM, doctor of technical sciences, professor
Yurkova A.I. _____

Consultant in the economic part Assoc. Prof., Candidate of Economic Sciences,
Narayevsky S.V _____

Consultant on labor protection and safety in emergencies Prof., Doctor of Economics,
Levchenko O.G _____

Normocontrol Consultant Assoc. Prof., Candidate of Technical Sciences, Trosnikova I.
Yu. _____

Reviewer:

Professor of the Department of Physical Materials Science and Heat Treatment, Doctor
of Technical Sciences, Professor, Makogon Yu.M. _____

I certify that in this master's dissertation
there are no borrowings from the works of other
authors without proper references.

Student _____

Kyiv - 2021

**NATIONAL TECHNICAL UNIVERSITY OF UKRAINE “IGOR
SIKORSKY KYIV POLYTECHNIC INSTITUTE”**

**E.O. Paton Institute of Materials Science and Welding
High Temperature Materials and Powder Metallurgy Department**

Education level	Second (master's)
Specialty	132 Materials science
Educational program	Nanotechnologies and computer design of materials

«Admission to the defence»
Head of the department
_____ I.I. Bogomol
«_____» ____ 2021

TASK

for the master's dissertation of the student

Shao Yiru

1. Topic of master's thesis: «Structure and mechanical properties of multicomponent AlNiCoFeCrTiMo alloy obtained by mechanical alloying and sintering», Research supervisor: professor, doctor of technical science Yurkova Alexandra Ivanovna, approved by order of the University of «19» November 2021 y. No 261/21-ci

2. The deadline for submission of the dissertation by a student is Dec. 15, 2021

3. Object of the research is AlNiCoFeCrTiMo alloy obtained by mechanical alloying and sintering.

4. Subject of the research is the structure and mechanical properties of AlNiCoFeCrTiMo alloy obtained by mechanical alloying and sintering.

5. List of tasks to be developed:

a) Literary review:

– To introduce the research status of contemporary world literary publications of high-entropy alloy and high-entropy alloy coatings

– To introduce the core effects of high-entropy alloys, the law of phase formation and the main properties of high-entropy alloys;

– To introduce the preparation methods and characteristics of high-entropy alloy

and high-entropy alloy coatings

- To introduce the application of high-entropy alloy and high-entropy alloy coating;

b) Experimental:

- To select and validate the chemical composition of high-entropy alloy;
- To prepare AlNiCoFeCrTiMo HEA by mechanical alloying in a planetary mill;
- To obtain solid HEA AlNiCoFeCrTiMo by spark plasma sintering, sintering under pressure;

- To investigate and compare the microstructure, phase, chemical composition and mechanical properties of HEA AlNiCoFeCrTiMo;

c) Discussion of the results:

- analyse the results and draw conclusions.

6. Approximate list of graphic (illustrative) material:

- topic of work, its actuality, purpose and main tasks;
- methods of obtaining high-entropy alloy powder and solid samples;
- selection and validation of research material;
- research methods (characterization techniques) for structure, phase composition of AlNiCoFeCrTiMo HEA powder and solid HEA AlNiCoFeCrTiMo;

- experimental data on the structure and phase composition of AlNiCoFeCrTiMo HEA powder and solid HEA AlNiCoFeCrTiMo;

- experimental data on the Vicker hardness of the solid HEA AlNiCoFeCrTiMo;;
- results and conclusions.

7. Approximate list of publications:

8. Date of issue of the assignment: 01.09.2021 y.

CALENDAR PLAN

item No	The name of the execution stages of Master's Thesis	The term of the practice stages	Note
1	A patent information search, analysis of literature data and writing a review	15.9.2020- 10.05.2021	
2	Select and validate the chemical composition of high-entropy alloy	10.09.2021	
	Fabrication of the high-entropy alloy powders by mechanical alloying in a planetary mill	20.09.2021	
4	Investigation of structure, phase and chemical composition of as mechanically alloyed HEA with SEM and XRD	27.09.2021	
5	Investigation of thermal stability of HEA powder with DSC and XRD analysis	10.10.2021	
	Production of compact samples by sintering	12.10.2021	
6	Investigation of structure, phase and chemical composition of sintering samples with SEM and XRD	14.10.2021	
8	Vickers hardness measurements and mechanical testing	15.10.2021	
9	Analysis and generalization of the obtained experimental results	30.9.2021- 30.10.2021	
10	Section of labor protection	30.10.2021- 10.11.2021	
11	Section of startup and economic	05.11.2021- 15.11.2021	
12	Report design	15.11.2021	

Undergraduate _____

Yiru Shao

Supervisor from the institution _____

Alexandra YURKOVA

ABSTRACT

The master's thesis contains: 120 pages, 15 figures, 17 tables, 107 sources.

HIGH ENTROPY ALLOY, MECHANICAL ALLOYING, MECHANICAL PROPERTIES, PHASE COMPOSITION, SINTERING, SOLID SOLUTION, POWDER, STRUCTURE

The purpose of the work is to study the structure and mechanical properties of AlNiCoFeCrTiMo HEA obtained by mechanical alloying and sintering. In order to achieve this purpose, the following tasks are solved:

- 1) The selection and justifying alloy powder compositions applying the phase formation empirical rules to obtain solid solutions in high-entropy alloys (determination of the mixing entropy; mixing enthalpy; the difference of atomic radii δ ; the valence electron concentration (VEC), and calculate the necessary batches.
- 2) Fabrication of the high-entropy alloy powders by mechanical alloying and study its structure and phase composition as well as thermal stability.
- 3) Selection the sintering method for conservation of nanostructure and phase composition in HEA after mechanical alloying; production compact samples.
- 4) Analyse the structure, phase and chemical composition, as well as mechanical properties.
- 5) Analyse the results of the experiment and draw conclusions.

Research methods and equipment:

The mechanical alloying was carried out in a planetary ball mill; Spraying was performed on a DYMET 405 setup. The structure and phase composition were studied using a scanning electron microscope, REMMA—106I and X-ray diffractometer, Ultima IV. The NETZSCH differential scanning calorimeter is used to measure the differential scanning calorimetry signal (DSC) curve of the HEA. Microhardness was determined by indentation on a PMT-3 and Micron Gamma machine.

Scientific novelty of the results:

Comparing the microstructure and mechanical properties of pressure sintering and SPS sintered HEA, it can be concluded that, the high-entropy alloy prepared by pressure sintering has better microstructure and high mechanical properties. Tests have proved that the AlNiCoFeCrTiMo high-entropy alloy prepared by MA-SPS has higher strength and hardness.

CONTENT

1 TECHNOLOGICAL SECTION	11
1. Literature review	11
1.1 The development of metal materials	11
1.2 History of high entropy alloys.....	12
1.3 Definition of high entropy alloy.....	13
1.4 The thermodynamic basis of high entropy alloys	14
1.5 The core effects in high entropy alloys	16
1.5.1 High-entropy effect	17
1.5.2 Slow diffusion effect	17
1.5.3 Lattice distortion effect	18
1.5.4 Cocktail effect	19
1.6 The structure and properties of typical high entropy alloys.....	19
1.6.1 Thermal stability of high entropy alloys	21
1.6.2 Mechanical properties of high-entropy alloys	23
1.6.3 Corrosion resistance of high-entropy alloys	25
1.6.4 Other functional performance	26
1.7 The application of high entropy alloys.....	27
1.8 The preparation method of high entropy alloy.....	27
1.8.1 Vacuum melting.....	28
1.8.2 Powder metallurgy	28
1.8.3 Mechanical alloying	29

1.8.4 Spark plasma sintering	31
1.9 HEA coatings processes production methods	35
1.9.1 Laser cladding	35
1.9.2 Thermal spray method.....	37
1.9.3 Cold spraying technology	39
1.10 Conclusions and main aims of thesis	40
2 EXPERIMENTAL MATERIALS AND PROCEDURES.....	41
2.1 The selection of alloy components.....	41
2.2 Preparation method for AlNiCoFeCrTiMo high entropy alloy	43
2.2.1 Preparation of HEA powder	44
2.2.2 Preparation of solid HEA	44
2.3 Characterization of microstructure and phase composition	48
2.3.1 X-ray diffraction analysis (XRD)	48
2.3.2 Scanning electron microscope	49
2.3.3 Thermal analysis	49
2.3.4 Vickers hardness.....	50
2.3.5 Mechanical testing.....	51
3 RESULTS AND DISCUSSIONS.....	52
3.1. Formation of structure and phase composition of equiatomic AlNiCoFeCrTiMo high- alloy during mechanical doping	52
3.2 Thermal stability of AlNiCoFeCrTiMo alloy obtained by mechanical alloying	56
3.3 Structure and phase composition of AlNiCoFeCrTiMo alloy after sintering.....	60
3.4 Mechanical properties of AlNiCoFeCrTiMo HEA after pressure sintering	63

4 LABOR PROTECTION SECION	65
4.1. Analysis of harmful and dangerous production factors	65
4.2 Engineering solutions to ensure occupational safety	67
4.2.1 Requirements for production facilities	67
4.2.2 Requirements for production buildings and sites.....	68
4.2.3 Ventilation requirements	69
4.2.4 Requirement of electrical safety.....	72
4.2.5 Requirement of fire safety.....	73
4.2.6 Labor protection conclusion.....	74
5 ENERGETICAL SECTION.....	76
5.1 Energy for research	76
6 ECONOMICAL SECION	77
6.1 Labor costs	77
6.2 Single social contribution.....	79
6.3. Materials required for research	79
6.4 Other direct uncalculated costs	81
6.5 Development of a planned calculation of the estimated cost of the topic	81
6.6 Scientific and technical efficiency of research.....	83
7 STARTUP SECTION	88
7.1 Introduction of startup	88
7.2 The contents and characteristics of the startup stage	91
7.3 Analysis of the competitive environment.....	94
7.4 Development of market strategy of the project.....	99

7.5 Conclusion..... 103

CONCLUSIONS 105

REFERENCES..... 107

1 TECHNOLOGICAL SECTION

1. Literature review

1.1 The development of metal materials

Since the existence of human civilization, in the development process of mankind for thousands of years, the development and application of new materials is closely related to the eternal pursuit. From the Stone Age to the Bronze Age, the development of materials also means the development of human civilization, science and technology. Among them, the development of metal materials plays an important role which can't be ignored. Social development is putting forward more stringent requirements on the performance of various materials—that is the reason why researchers from all over the world are also committed to researching methods and trying to obtain various metal materials with excellent performance. So far, there are about 30 kinds of metal alloys developed by mankind. At present, two methods are often used to obtain metal materials with excellent properties. First way is the improvement of the preparing process, such as rapid solidification [1], electron beam physical vapor deposition method [2], semi-solid forming [3],[4], etc.; the second method is adding of the trace elements and composition adjusting to obtain materials with different properties, such as amorphous alloy materials[5], metal matrix composite materials[6] and so on.

At present, the development of traditional alloy systems has approached saturation, and it seems more and more difficult to create new alloy systems based on traditional alloy design concepts. As the industrial development puts forward higher and higher requirements for material properties, it is urgent to break through the traditional alloy

design concepts and develop new materials and new alloy systems. However, past development experience tells us that the main reason why alloys cannot develop in a multi-directional direction is that although we can improve performance by adding a small amount of alloying elements, due to limited solubility, too many types or quantities of elements will lead to a large number of brittle metals. The formation of inter-compounds and other complex phases deteriorates the properties of the alloy, and also brings great difficulties to the organization and composition analysis of the material.

1.2 History of high entropy alloys

The discovery of high-entropy alloys can be traced back to the "confusion principle" put forward by Professor Greer in Cambridge in 1993. The principle is that the more elements alloy is consist then easier it forms amorphous alloys [7]. This principle provides a way for the design of amorphous alloys by increasing the number of elements and the confusion in the alloy.

In 2004 the series of alloys from 16 and 24 elements with equal atomic ratio were fabricated using copper mold casting by Oxford professor B. Cantor. This series of alloys show crystalline structure which indicates that the number of elements is not the only factor that determines the structure of the alloy [8].

In the same year, the concept of "high-entropy alloy" was put forward by Jien-Wei Yeh which marked the beginning of high-entropy alloys researches. Since it was first reported[13], high-entropy alloys have gradually become a frontier and hot research direction in the field of materials while the number of related research results has been

increasing years by years.

Due to the unique structural composition of high-entropy alloys, this kind of alloys have some excellent properties that traditional alloy materials cannot match, such as excellent mechanical properties [9], catalytic properties [10], radiation resistance [11], and corrosion resistance [12] and so on. It can be seen that high-entropy alloys have unlimited application potential.

1.3 Definition of high entropy alloy

At present, there are two main ways to define high-entropy alloys, which are based on composition and based on mixed entropy. The first way which can definite high-entropy alloy as a class of materials that consists 5 or more elements where the atomic percentage of each element is between 5% and 35% [13]. To clarify the definition of the latter, we need to understand the relationship between the mixing entropy and the alloy system. According to the assumption of the relationship between entropy and system complexity proposed by Boltzmann, N kinds of elements are mixed with equal atomic ratio to form a solid solution, and the system entropy change can be expressed as [14]:

$$\Delta S_{\text{conf}} = -K \ln W = -R \ln N, \quad (1.1)$$

where N , K , W , R are the kinds of elements, Boltzmann's constant, degree of mixing and gas constant ($8.314 \text{ J} / (\text{K} \cdot \text{mol})$), respectively.

According to this definition, the entropy of mixing increasing exponentially to number of elements in system.

Jien-Wei Yeh and et al. [15] believe that $\Delta S_{\text{conf}} = -1.5R$ is a necessary condition for atoms to resist the bonding force at high temperatures, so $\Delta S_{\text{conf}} = -1.5R$ can be used as the boundary between medium-entropy alloy and high-entropy alloy which mixing entropy are $-1.38R$ and $-1.61R$, respectively. According to this, alloys can be divided into three categories: low-entropy alloys composed from one or two elements, namely traditional alloys ($\Delta S_{\text{conf}} \leq R$); medium-entropy alloys composed from two to four elements ($\Delta S_{\text{conf}} \leq 1.5R$); a high-entropy alloy composed with at least five elements ($\Delta S_{\text{conf}} > 1.5R$).

In subsequent studies, some researchers have extended the definition of high-entropy alloys. So, some alloy four or more elements and non-equal molar ratio can still be classified as high-entropy alloys [16]. Moreover, due to non-equal molar ratio alloys have better comprehensive properties than equilibrium high-entropy alloys, that's why the non-equal molar ratio alloys have been more studied.

1.4 The thermodynamic basis of high entropy alloys

"Entropy" was first proposed by the German physicist Clausius, who used it as a parameter to characterize the degree of chaos in the system in thermodynamics. The larger the entropy value is, the more chaotic the system will be. If the contribution of atomic vibration to the entropy of the system is ignored, the entropy value in the high-entropy alloy mainly reflects the arrangement of atoms. In high-entropy alloys, the entropy value

of the system mainly refers to the atom mixing entropy ΔS_{mix} . From the thermodynamic formula, the relationship between the Gibbs free energy G , enthalpy H , absolute temperature T and entropy S is as follows: $G = H - TS$ [17]. Also,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}, \quad (1.2)$$

where ΔH_{mix} is the enthalpy of binary mixing, which can be calculated by the following formula:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n (4\Delta H_{mix}^{AB})_{ij} c_i c_j, \quad (1.3)$$

where c_i is the atomic percentage of the i -th element while ΔH_{mix}^{AB} represents the binary mixing enthalpy of the two atoms A and B .

It can be seen from (1.2) that the free energy of the alloy system is affected by mixing entropy, mixing enthalpy and mixing temperature. The enthalpy of mixing promotes the formation of compounds and causes the alloy to become brittle; the entropy of mixing promotes the formation of solid solutions and makes the organization more stable. Compared with intermetallic compounds, the amount of Gibbs free energy change required for the formation of solid solutions is lower—which inhibits the formation of complex intermetallic compounds in the alloy, and promotes simple solid solutions formation.

According to the Hume-Ruthery rule, the difference in atomic size is also an important factor affecting the formation of high-entropy alloys. The difference in atomic

size of elements contained in high-entropy alloys can be defined as:

$$\delta = \sqrt{\sum_{i=1}^N c_i \left(1 - \frac{r_i}{\sum_{i=1}^N c_i r_i}\right)^2}, \quad (1.4)$$

where r_i is the atomic radius of component i .

It is known that ΔS_{mix} is a parameter that determines the uniformity of the spatial distribution of particles, while ΔS_{mix} is related to the segregation of particles. When ΔS_{mix} is positive, particles i and j repel each other, and when ΔS_{mix} is negative, particles i and j particles attract each other. Therefore, some scholars have proposed that the parameter Ω comprehensively reflects the effects of mixing enthalpy and mixing entropy, and its calculation formula is as follows:

$$\Omega = T_i \Delta S_{\text{mix}} / \Delta H_{\text{mix}}, \quad (1.5)$$

In formula (1.5), T_i is the alloy liquidus temperature.

1.5 The core effects in high entropy alloys

Due to the complexity of its composition, high-entropy alloys are generally considered to have four major characteristics: high-entropy effect (thermodynamics characteristic), slow diffusion effect (kinetics characteristic), lattice distortion effect (structure characteristic) and "cocktail" effect.

1.5.1 High-entropy effect

The most important effect of high-entropy alloys is the high-entropy effect. If the alloy system wants to achieve the most stable state, its Gibbs free energy is required to be at the lowest level. When the number of elements in the high-entropy alloy is large enough and the mixing entropy in the system is greater than the entropy change required to form intermetallic compounds, the high-entropy effect will inhibit the appearance of intermetallic compounds and promote the mixing of components to form a simple BCC or the FCC structure reduces the Gibbs free energy of solid solution formation, thereby inhibiting the segregation and combination of elements. Therefore, high-entropy alloys usually form a simple solid solution phase.

1.5.2 Slow diffusion effect

The phase formation in HEA is significantly depends on the diffusion of atoms. Since high-entropy alloys have many basic components, it requires cooperative diffusion between the components to achieve the equilibrium separation of different phases. This necessary cooperative diffusion, as well as the lattice distortion that hinders the movement of atoms, will limit the effective diffusion rate in high-entropy alloys. In the casting process of high-entropy alloys, the phase separation during cooling is usually suppressed in the high temperature range and delayed to the low temperature range. Therefore, the atomic properties of each component are quite different. The content of each metal

element is equivalent and the elements have complex interactions, which leads to relatively slow diffusion of elements during the alloy solidification process. Therefore, a simple solid solution structure is retained which delays the nucleation and growth of precipitates while promotes the formation of a nano-sized phases [17]-[21].

1.5.3 Lattice distortion effect

In a multi-principal high-entropy alloy different types of distributed around the some and have different atomic radii which resulting in a large stress and severely distortion of the crystal lattice. This idea may be rooted into the hard sphere model, as schematically shown in Figure 1.1. Also, since there are many kinds of elements in the high-entropy alloy, its solid solution structure is very different from the traditional solid solution structure. In addition, the difference in binding energy and crystal structure between different kinds of atoms can also cause serious distortion of the crystal lattice [24].

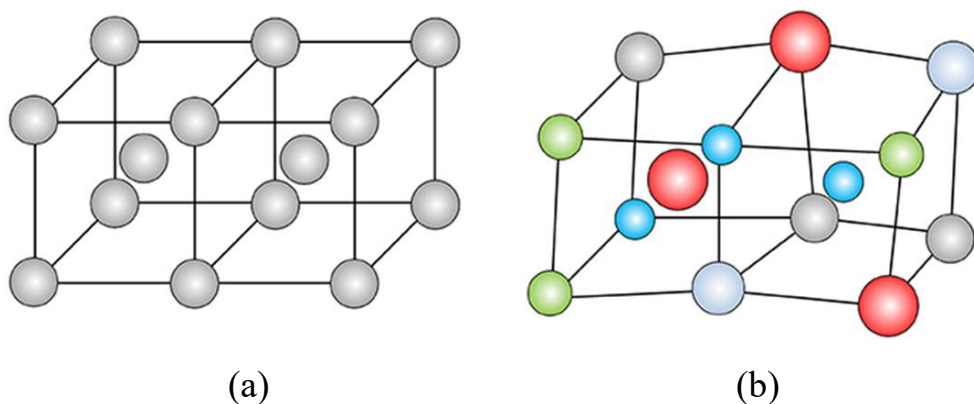


Figure 1.1 – The illustrations of (a) a perfect BCC lattice in pure metals and (b) a distorted BCC lattice in multicomponent alloys[24].

The high lattice distortion of high-entropy alloys will significantly affect on its such properties as hardness, strength, thermal resistance, electricity conductivity and et al.

1.5.4 Cocktail effect

The "cocktail" effect was first proposed by the Indian scholar Ranganathan [22]. The "cocktail" effect of high-entropy alloys means that the interaction between the multiple elements allows create the alloy which have the basic characteristics of each elementary element without their disadvantages. For example, the addition of Al element with FCC structure often promotes the formation of the BCC solid solution structure in alloy and increases the hardness [23]-[24].

1.6 The structure and properties of typical high entropy alloys

The three typical structures of high-entropy alloys include FCC, BCC and HCP structures. In addition, there are some two-phase or multi-phase high-entropy alloys, such as eutectic alloys (FCC and BCC), precipitation-strengthened alloys (FCC+L12, BCC+B2, FCC+Laves/ σ/μ , etc.), dual-phase alloys (FCC+BCC, FCC+HCP, etc.) and et al. Single-phase FCC structure high-entropy alloys include equilibrium alloys and non-equilibrium alloys. The equilibrium high-entropy alloys include such alloys as CoCrFeMnNi, CoCrFeNi, PdFeCoNi, etc. The non-equilibrium high-entropy alloys

include such alloys as $\text{Co}_{20}\text{Cr}_{26}\text{Fe}_{20}\text{Mn}_{20}\text{Ni}_{14}$ 、 $\text{Fe}_{40}\text{Mn}_{40}\text{Co}_{10}\text{Cr}_{10}$ 、 $\text{Al}_x\text{CrFeCoNi}$ ($x \leq 0.3$), $\text{Fe}_{40}\text{Mn}_{27}\text{Ni}_{26}\text{Co}_5\text{Cr}_2$, etc. Among them, the equilibrium CoCrFeMnNi high-entropy alloy is the first synthesized single-phase FCC structure alloy, and called as "Cantor" alloy. In this alloy all five components of the alloy are uniformly distributed without component segregation and form stable structure with good plasticity at room temperature as same as liquid nitrogen temperature. So, it's has become the most widely studied high-entropy alloy with FCC structure.

The structure of high-entropy alloys currently studied are mainly FCC and BCC solid solution structures, but some scholars have also studied and prepared high-entropy alloys with HCP phase as the main phase. Figure 1.2 show comparison between hardness of high-entropy alloys with different types of structure as same as comparison between high-entropy alloys and their constituent elements[27].

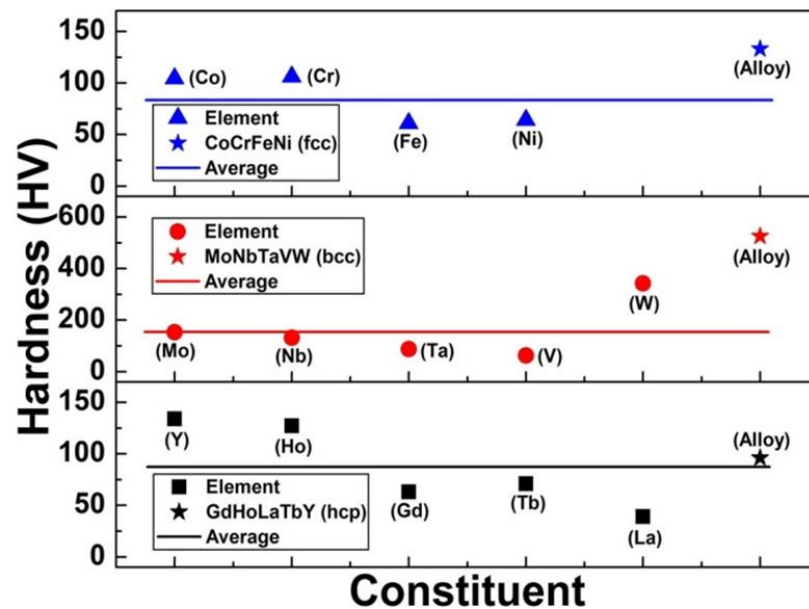


Figure 1.2 – The comparison between hardness of three kinds of high entropy alloys and their constituent elements [27]

It can be seen from the figure that BCC and FCC metals have obvious solid solution strengthening effects, while there is no obvious solid solution strengthening effect in the metal HCP.

High-entropy alloys are not only simple in phase composition but also have fine grains which tend to formation of nanocrystalline or amorphous. During the mixing process of each component, a large amount of mixing entropy is stored at the grain boundary which expands the solubility range of the terminal solid solution existence, and becomes the moving force for formation of solid solution. At the same time, due to the variety of elements and chaotic arrangement, the formation involves the diffusion and redistribution of multiple elements, which leads to the delay of the nucleation and growth of precipitates while simultaneously promoting the formation of nanophases. In addition, if the difference in atomic size is large enough, the distorted lattice will be too high to maintain the crystal configuration due to the lattice distortion energy, which will collapse to form an amorphous phase.

The unique alloy design concept and special structural characteristics of high-entropy alloys give them some special properties that are different from traditional alloys.

1.6.1 Thermal stability of high entropy alloys

Thermal stability usually refers to the heat resistance of the alloy, that is, the ability of the alloy to maintain its own properties at higher temperature which reflects the length of working hours of materials at high temperatures, and has great significance to modern

industry. According to the Gibbs free energy relationship, it can be seen that a larger $T\Delta S_{\text{mix}}$ helps to reduce the free energy of the system which is important for high entropy alloys with large ΔS_{mix} value. Therefore, with increasing of the temperature T , in the multicomponent system seems to be more stable. So, many high-entropy alloys can maintain high strength and hardness at high temperatures [28], which is shown in figure 1.3. The high-temperature oxidation resistance of some high-entropy alloy coatings is equivalent to that in high-quality nickel-based thermal barrier coatings, especially when the temperature is above 800 °C.

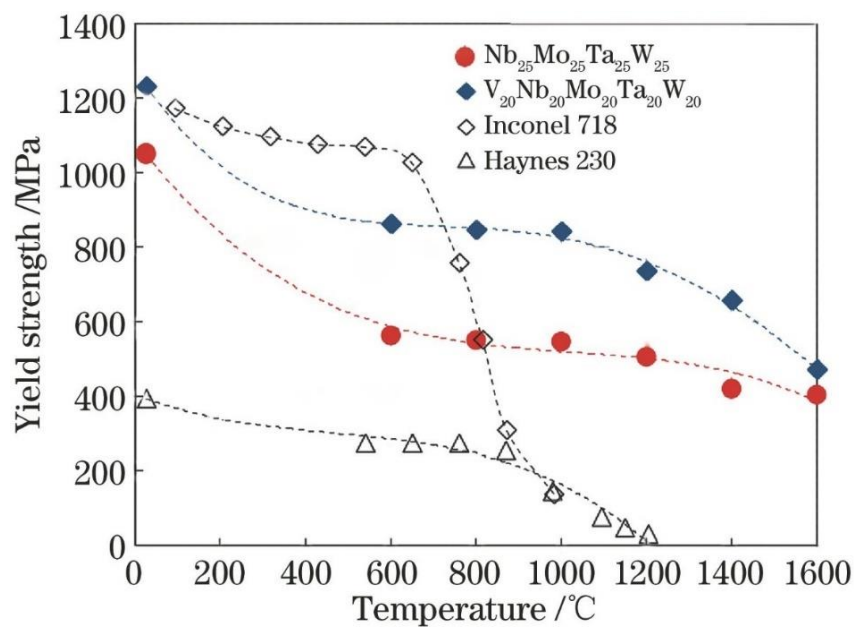


Figure 1.3 – Comparison of high-temperature compression performances of high-melting-point and high-entropy alloys and traditional nickel-based high-temperature alloys [28]

Nong and et al. [30] studied the thermal stability of the AlCrFeNiTi high-entropy alloy and found that after being heating up to 400-900 °C and held for 0.5-10 h with next

air cooling alloy – mostly maintained the original structure, and yield strength was maintained at 4000 MPa which shows good thermal stability of alloy. Wang and et al. [31] found that the MoNbTaTiV high-entropy alloy powder prepared by mechanical alloying still maintains good thermal stability at 1200 °C because powder is refined and the lattice stress is weakened are observed.

1.6.2 Mechanical properties of high-entropy alloys

For traditional alloys with one principal element, the Young's modulus and other characteristics firstly reflects the intrinsic characteristics of the principal element. For example, the Young's modulus of traditional nickel, titanium and aluminum alloys are about 200, 110 and 75 GPa, respectively while the adjustable range of value is limited close to these values. In contrast, a study of high-entropy alloys has shown that their specific strength is much difference from traditional alloys while the modulus has a large distribution range (fig. 1.4) [29].

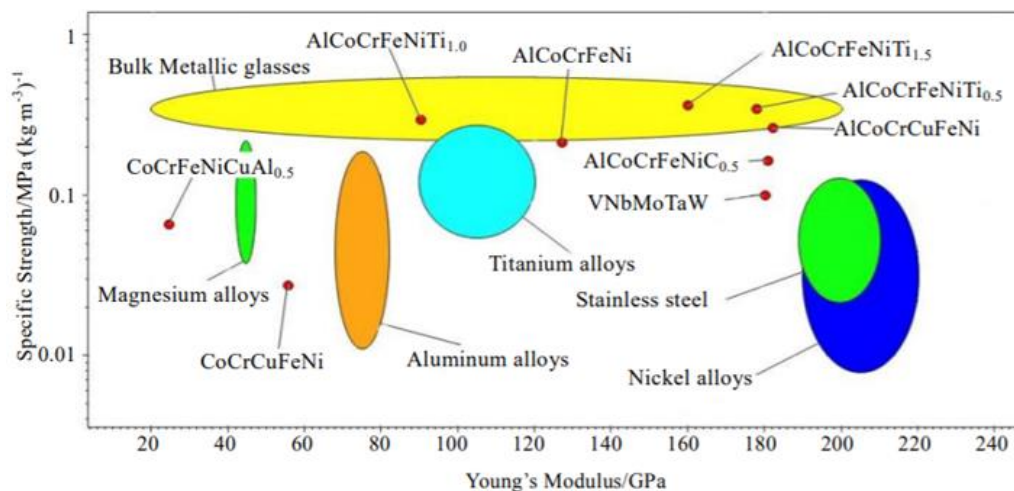


Figure 1.4 – Specific strength and Young's modulus of traditional alloy and HEAs [29]

Due to its special structure, high-entropy alloys have excellent mechanical properties. Figure 1.5 shows the tensile properties of some transitional and refractory high-entropy alloys. From the figure 1.5, we can find that the mechanical properties of 3d transitional high-entropy alloys gradually decrease with increasing temperature while their strength is generally lower than that of refractory high-entropy alloys.

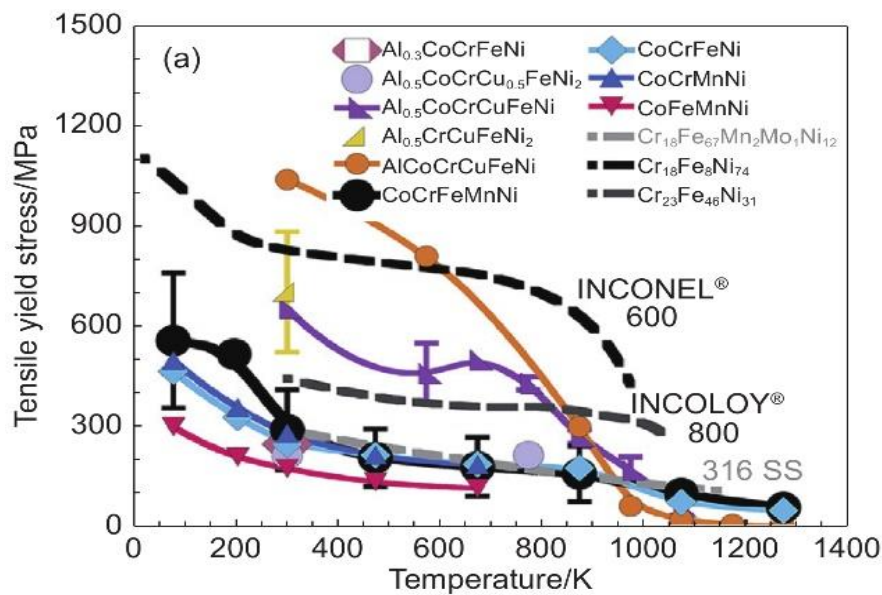


Figure 1.5 – Strength-temperature curves of typical high entropy alloys [34]

Also, with the increasing of temperature, their strength decreases faster than that in refractory high-entropy alloys. The mechanical properties of alloys are generally affected by three factors:

a) the addition of alloying elements. The alloying elements will cause lattice distortion and phase changes in alloy while take an important role in solid solution strengthening mechanisms [31];

b) change of strain rate. The alloy strain rate directly affects the stress and strain

during its deformation stage [32];

c) use of deformation and heat treatment processes, which has directly effect on the structure and mechanical properties of the alloy [33];

1.6.3 Corrosion resistance of high-entropy alloys

The corrosion resistance mechanism of high-entropy alloys can be summarized by the following points:

a) high-entropy alloys tend to form a single solid solution or amorphous phase due to their high-entropy effect. As a result, the composition of the alloy is more homogeneity. A single solid solution or amorphous phase can weaken the effect of galvanic corrosion as same as reduce the number of micro-batteries, and improve the corrosion resistance of the alloy;

b) the surface of the high-entropy alloys coatings with such elements as Al, Cr, Ni, Ti and Mo are forming a passive film which reduces the corrosion rate of the material;

c) compared with bulk high-entropy alloys, coating alloys have no time to diffuse due to the rapid quenching technology during the preparation process, so that the alloy components are distributed more uniformly, thereby improving the corrosion resistance of the alloy.

Qiu [36] et al. studied the effect of Ti on the corrosion resistance of $\text{Al}_2\text{CrFeNiCoCu}$ high-entropy alloy coatings, and found that compared with Q235 steel, the self-corrosion current density of the alloy coating was reduced by about 2 orders of magnitude, at 0.5 mol/L HNO_3 The corrosion resistance in the solution is improved. Qiu [37] et al. studied

the structure and corrosion properties of $\text{Al}_x\text{CoCrFeNiTi}_y$ high-entropy alloy and found that the alloy system has higher corrosion resistance. In 0.6M NaCl solution, its corrosion resistance is better than stainless 304L steel. Cyclic potential polarization indicates that the studied HEAs undergo pitting corrosion after breakdown.

1.6.4 Other functional performance

At present, the research on high-entropy alloys mainly focuses on the traditional performance but there are few researches on the other specific functional properties of high-entropy alloys (such as catalytic performance, radiation resistance, superconductivity and et al [38]-[41]).

Bi[42] and Gromilov[43] prepared $\text{Ni}_{20}\text{Fe}_{20}\text{Mo}_{10}\text{Co}_{35}\text{Cr}_{15}$ and $\text{Ir}_{19}\text{Os}_{22}\text{Re}_{21}\text{Rh}_{20}\text{Ru}_{19}$ bulk high-entropy alloys by arc smelting. They studied the hydrogen evolution reaction and the methanol electrooxidation catalytic reaction at room temperature, respectively, and found that the bulk high-entropy alloys can also have good catalytic activity.

Xia and et al. [44] studied the changes of $\text{Al}_x\text{CoCrFeNi}$ alloy under high radiation damage and found that the alloy structure and phase composition not changes which indicating about the ability of this alloy to resist radiation damage.

Gou and et al. [47] studied the $(\text{TaNb})_{0.67}(\text{HfZrTi})_{0.33}$ high-entropy alloy and found that the superconducting transition temperature of the alloy under normal pressure is 7.7 K. When the pressure increases from 60 GPa to 190.6 GPa, the transition temperature changes from 10 K drops to 9 K. It shows that the alloy has the potential as a superconducting material under high pressure conditions.

1.7 The application of high entropy alloys

In the research process of high-entropy alloys, people have also developed other high-entropy materials, such as high-entropy superalloys, high-entropy metallic glasses, high-entropy carbides, high-entropy nitrides, and high-entropy oxides [45]. All these materials have great potential application value, for example, manufacturing machine parts, molds, corrosion-resistant parts, cutting tools, functional coatings, diffusion barriers and high-temperature structural parts [46]. So, only by thoroughly studying basic scientific issues and accumulating a wealth of knowledge and experience we can develop more high-entropy materials with excellent properties.

1.8 The preparation method of high entropy alloy

At present, there are many preparation methods of high-entropy alloys which can be classified according to different sample shapes: bulk, powder, coating, film, foil, and composite high-entropy alloys. Figure 1.6 shows the research and preparation methods of samples with different shapes[48].

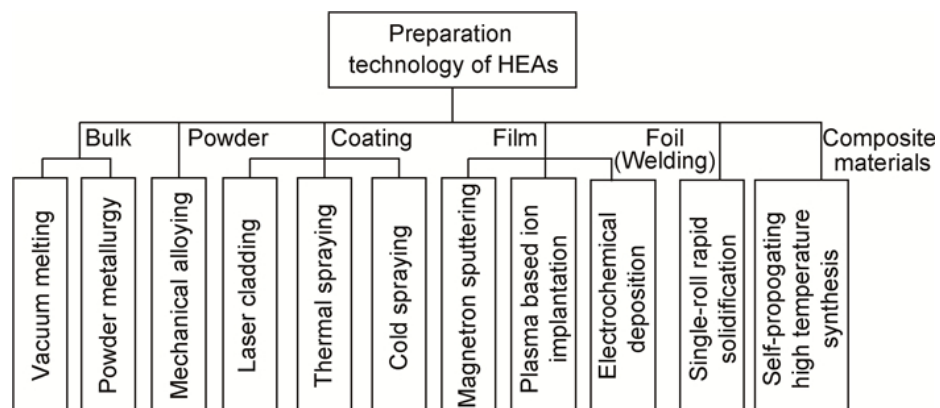


Figure – 1.6 Preparation technology of HEAs [48]

1.8.1 Vacuum melting

The vacuum melting method is currently the most widely used method in research. It is divided into two types: vacuum induction melting and vacuum arc melting. The main processes of vacuum melting method for preparing high-entropy alloys are: putting pure metal into a crucible, filling it with argon gas after vacuuming, smelting under the protection of argon gas and casting it into shape. This method is currently used by most researchers to prepare high-entropy alloys. Its smelting temperature is high, it can smelt alloys with a higher melting point, and it has a good effect on the removal of volatile impurities and certain gases [49]. Vacuum arc smelting uses arc heat to melt metal. Since smelting under vacuum can easily reduce the nitrogen, hydrogen, oxygen and other elements dissolved in the metal to a lower level, it can significantly improve the smelting quality of the alloy.

However, high-entropy alloys prepared by vacuum melting often have defects such as uneven structure, pores, shrinkage, large internal stress, and large brittleness, which make it difficult to maximize the performance of high-entropy alloys and limit the further application of alloys.

1.8.2 Powder metallurgy

Powder metallurgy is a method that uses metal or non-metal powder as raw materials, presses them into shapes and then sintering to final products [50]. The powder interacts during the pressing process, causing plastic deformation and work hardening,

thereby increasing the surface activity of the alloy. Powder metallurgy has a high reproducibility and easy forming as well as the homogeneity of the alloy structure and the accuracy of its composition which can be used to prepare some metals and alloys with higher melting points without segregation of its components. The disadvantage of this method is difficulty to dense compact of materials, especially hard materials, which leads to the existence of voids in the product. Also, significant influence on compacting have particles size. So, large particles are difficult to mix while too small particles decrease compact ability of powder [51].

The GUAN and et al.[52] prepared AlNiCrFe-CuMo_x (x=0~0.2) high-entropy alloy by powder metallurgy and studied the influence of Mo on alloy microstructure and mechanical properties of the alloy. It is founded that increase of Mo can promote the formation of FCC phase while alloy with Mo content x=0.1 has highest hardness and strength.

Zhao Ruifeng and et al.[53] prepared AlCrMn-MoNiZr and AlCrMnMoNiZrB_{0.1} high-entropy alloys by powder metallurgy technology, and found that the microstructures of the two alloys are both Cr-rich and Mo-rich BCC phases with intermetallic compounds. At the same time, the alloys are stable at high temperatures with good performance and high hardness.

1.8.3 Mechanical alloying

Mechanical alloying is mixing of the feedstock using high-energy ball mill. During this process, the powder undergoes mechanical changes such as cold welding, fracture

and plastic deformation which are repeat at all process time. Figure 1.7(a) shows a schematic diagram of the alloying process [54]. This method can effectively control the phase composition and microstructure of the alloy, and is an effective way to prepare dispersion strengthened materials.

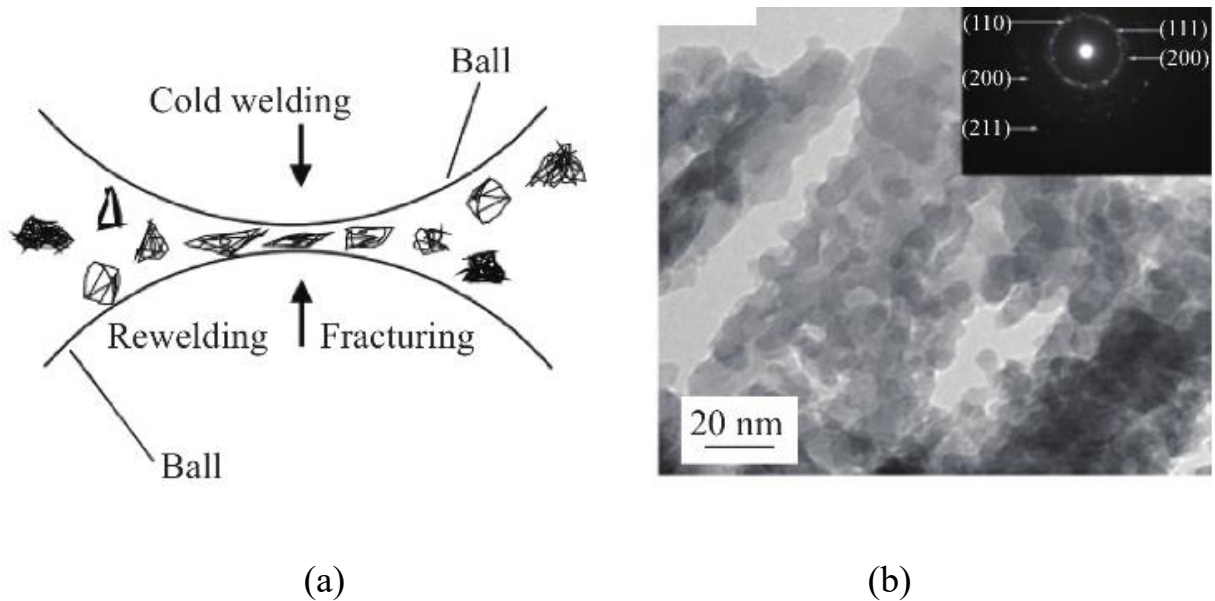


Figure – 1.7 Schematic of the alloying process (a); transmission electron microscopy (TEM) image and selected-area diffraction (SAED) pattern of CoCrFeNiMn HEA powder milled for 60 h (b) [53]

Wang and et al.[55] prepared CoCrFeNiMn high-entropy alloy powder by mechanical alloying method then used transmission electron microscope (TEM) and X-ray diffraction (XRD) for observation and analysis. They founded that the alloy has a nanostructure as well as exhibits good thermal stability and mechanical properties.

At present, mechanical alloying has been widely used in the preparation of multi-principal high-entropy alloy materials. For example, Zhang and et al. [56] used a

mechanical alloying method to prepare AlCrFeNiCuCo high-entropy alloy with BCC+FCC crystal structure and grain size of 7 nm. Fu and et al.[57] successfully prepared a single-phase FCC structure $\text{Co}_{25}\text{Ni}_{25}\text{Fe}_{25}\text{Al}_{7.5}\text{Cu}_{17.5}$ high-entropy alloy through mechanical alloying and spark plasma sintering, with a compressive yield strength of 1795 MPa and a hardness of 454 HV. Yang and et al.[58] used mechanical alloying and spark plasma sintering to prepare a high-entropy alloy composite TiC/Al_{0.3}FeNiCo_{1.2}CrCu with a compressive yield strength of 1730 MPa, a plasticity of 29.5%, and a hardness of 645 HV.

The high-entropy alloy prepared by the mechanical alloying method has a stable microstructure, excellent room temperature processability and chemical homogeneity without component segregation and negative eutectic phenomena. In addition, the method also has the advantage of being able to prepare products with large differences in the melting points of raw materials. However, because mechanical alloying is a solid-state processing technology, due to wearing of ball milling media and balls as well as the influence of gas atmosphere, this method will inevitably introduce impurities such as O, N, Fe/WC. The introduced impurities may also react with the powder during ball grinding to form a new phase. Impurity pollution can change the phase composition and structure of the alloy and reduce the plasticity and toughness of the alloy. Therefore, the ball grinding process must be strictly controlled and reduce the contamination of powder.

1.8.4 Spark plasma sintering

Spark Plasma Sintering (SPS) is a fast, low-temperature, and environmentally

friendly new material forming technology, and it is one of the important methods for preparing high-entropy alloys. Its main feature is to activate the surface of the internal particles of the sintered body through the instantaneous discharge plasma. It has the advantages of fast heating rate, short sintering time, simple and convenient operation, low energy consumption, etc., so it has high thermal efficiency and easy to obtain compact sintering with fine grains. Body, is a new sintering technology with important practical significance and broad prospects[59].

SPS technology can be traced back to the beginning of the 20th century, when the United States first proposed the concept of current-assisted sintering[60]. In 1966, Inoue[61] invented the spark plasma sintering technology and applied for a patent. In the following 20 years, spark plasma sintering technology has been continuously improved, and Japanese companies have taken the lead in manufacturing a relatively complete spark plasma sintering system and put it into application.

Spark plasma sintering has a very fast sintering rate, which can complete the sintering within a few minutes, inhibit the growth of crystal grains, and retain the nanostructure of the precursor powder. The sintered bulk material has low electrical transport performance while maintaining good electrical transport performance. The thermal conductivity. Therefore, spark plasma sintering has become a common sintering technology for the preparation of high-performance, low-heat thermal conductivity electrical materials. In this experiment, "FAST" Type HP D 25(SPS-"FAST" Type HP D 25, German) [62] was used to prepare samples.

Before sintering, the raw material powder is loaded into the graphite mold and compacted with two graphite presses. For better electrical contact performance and

release, a layer of graphite carbon paper is usually placed between the powder raw material and the graphite press; After placing the graphite mold with the assembled raw material into the discharge plasma sintering furnace cavity, axial pressure (10 to 100 MPa) is applied with the pressure head at the upper and lower ends respectively, and the sintered powder is introduced into the pulsed DC of low voltage (5 V) and high current (0 to 1500 A) under vacuum closure conditions. Large pulsed direct current makes the raw material powder instantaneously produce a large amount of joule heat, so the heating rate is very high, in a very short period of time to achieve heating, insulation and cooling sintering process[63]. The fast discharge plasma sintering process is conducive to the maximum retention of micron/nanostructures of mechanically alloyed precursor powders, which is important for reducing the thermal conductivity of the material.

The main factors affecting the discharge plasma sintering technology are sintering temperature and temperature rise and fall rate, sintering pressure and atmosphere, current and sintering rate. The temperature of discharge plasma sintering directly affects the degree of density and grain refinement of the sample. The pressure and decompression of sintering also affect the microstructure of the sample, thus affecting the performance of the sample[64].

Mechanical alloying combined with spark plasma sintering technology can significantly improve the mechanical properties of materials. The research of Pan et al. [64] showed that the n-type and p-type Bi₂Te₃ bulk samples prepared by mechanical alloying combined with spark plasma sintering technology, compared with commercial zone smelting method samples, their mechanical strength increased by about 2 times, the microscopic Vickers hardness has increased by 60%. Ji et al. [66] prepared CoCrFeMnNi

alloy by mechanical alloying method-spark plasma sintering (MA-SPS), and studied the alloying behavior and magnetic properties of the alloy. After 60 h of ball milling, the CoCrFeMnNi alloy has a simple structure of BCC+FCC phase. The research results show that in the SPS sintered alloy, there are two FCC structures with similar unit cell parameters but different grain sizes. The sintered alloy has a high compressive strength of 1987 MPa. An interesting magnetic transition process was discovered during the SPS sintering process. The magnetic transition is related to the coarsening of the structure and phase transition after sintering. Varalakshmi et al. [67]-[68] prepared CuNiCoZnAlTi and AlFeTiCrZnCu high-entropy alloys by mechanical alloying, and studied their structure and properties. Wei Ting et al.[69] also used the mechanical alloying method to prepare AlFeCrCoNi high-entropy alloy and studied its properties at different annealing temperatures.

In general, compared with the high-entropy alloy prepared by the casting method, the high-entropy alloy prepared by the powder metallurgy method usually has the advantages of fine grain, high strength, and high hardness, but the plasticity is poor. However, mechanically alloyed high-entropy alloy powders can be prepared by adopting a reasonable sintering process to produce high-entropy alloy blocks with more uniform composition and larger sizes, which provides more methods and approaches for the development and application of high-performance high-entropy alloys. At present, the structure and properties of mechanically alloyed AlNiCoFeCrTiMo high-entropy alloys have not been systematically and thoroughly studied. The effects of different element contents and other alloying elements in the alloy system on the structure and properties of the alloys are rarely reported. The AlNiCoFeCrTiMo high-entropy alloys There is also

less research on composite materials based on it. Using mechanical alloying combined with spark plasma sintering (MA-SPS) to prepare AlNiCoFeCrTiMo high-entropy alloys can improve the uniformity and accuracy of the alloy composition. At the same time, studying the structure and properties of the AlNiCoFeCrTiMo high-entropy alloy prepared by the "MA-SPS" method not only has positive academic research significance, but also has important practical application value.

1.9 HEA coatings processes production methods

It is well known that the high cost of high-entropy alloys due to their high alloy content is one of the main problems that limit the application of bulk materials. Therefore, scholars hope to reduce costs by preparing high-entropy alloy coatings or films. Therefore, with years of research on high-entropy alloy coating methods, the current preparation methods used in high-entropy alloy coatings mainly include laser cladding technology, thermal spray technology, and cold spray technology.

1.9.1 Laser cladding

Laser cladding is a surface modification technology. It uses a high-energy density laser beam to fuse cladding material with thin layer of the substrate to form a metallurgical bond between surface of the substrate and coating[59]. Zou [71] used laser cladding method to prepare CrNiAlCoMoB_x high-entropy alloy coatings on 45 steel substrates, and studied the influence of laser cladding process parameters and B content on coating

quality, microstructure and structure. The alloy coating is well combined with the substrate, uniform, compact and has high hardness, good corrosion resistance, excellent friction and wear performance.

An [72] used laser cladding technology to prepare $\text{Ti}_x\text{FeCoCrWSi}$ high-entropy alloy coating on the surface of 45 steel and found that $\text{Ti}_x\text{FeCoCrWSi}$ coating is mainly composed of dendrites. The average hardness of the alloy coating improving from 500 HV to 800 HV with increasing of Ti content while the wear rate increases and the wear resistance becomes worse.

Li and et al. [73] used laser cladding to prepare $\text{FeCoNiMnMoB}_{0.5}$ high-entropy alloy coatings with different Mo content on the Q235 steel substrate, focusing on the effect of Mo on the structure and properties of high-entropy alloys. The structure of this high-entropy alloy is dendritic, mainly composed of FCC phase and a small number of intermetallic compounds; in addition, with the increase of Mo content, the hardness of the alloy coating increases. Wen and et al. [74] prepared $\text{AlCoCrCu}_{0.5}\text{FeMoNiTi}$ high-entropy alloy coating by vacuum laser cladding. The alloy has good thermal stability. The hardness of the cladding alloy reaches 1 080 HV. After annealing at 500 °C, the coating hardness decrease, then increase the annealing temperature, the change of hardness is very small, after the temperature of annealing increasing to 900 °C, the hardness still reaches 943 HV. Gou and et al. [75] prepared the FeNiCoAlCu high-entropy alloy coating by laser cladding and found that the coating has good thermal stability and wear resistance below 780 °C.

The laser cladding method to prepare high-entropy alloy coatings has the following advantages:

- a) in theory, any high-entropy alloys can be used for coating;
- b) the composition of the alloy can be changed at will to obtain different coatings;
- c) a large difference between the melting point of the base metal and the alloy of the cladding layer not difficult cladding.

Although the laser cladding technology to prepare high-entropy alloy coatings has many advantages, based on the characteristics of this technology, its composition system cannot completely copy the design concept of bulk high-entropy alloys. The coating system for laser cladding high-entropy alloys and the design of coatings that take into account a variety of excellent properties are currently urgently needed to be studied in the preparation of high-entropy alloy coatings by laser cladding.

1.9.2 Thermal spray method

Thermal spraying is a method in which the coating material is heated to a molten state by a heat source, and then sprayed on the surface of the substrate and deposited to form a coating [76]. This coating preparation process can limit the segregation of elements, inhibit the nucleation and growth of intermetallic compounds, and promote the formation of a single solid solution [77].

Huang and et al. [78] first prepared $\text{AlCrFeMo}_{0.5}\text{NiSiTi}$ and $\text{AlCoCrFeMo}_{0.5}\text{NiSiTi}$ high-entropy alloy coatings with a thickness of about 200 μm by thermal spraying technology in 2004. This study found that the thermal spraying method can be used to obtain high-entropy alloys coatings but they have many defects.

Ang and et al. [79] used mechanical alloying method to obtain high-entropy alloy

nano-powder and then deposited AlCoCrFeNi and MnCoCrFeNi coatings by plasma spraying method. The coating structure is a simple FCC and BCC solid solution dual phase with low porosity, uniform structure and the highest hardness which reach 4.42 GPa. This is because high-entropy alloy nano-powders are easier to diffuse in molten state, filling the defects. So, this preparation method reduces defects quantity that's why coating has more excellent performance.

Today, atmospheric plasma spraying (APS) technology has been widely used in the preparation of high-entropy alloy coatings. This process has high flame temperature, energy concentration, high bonding strength, high deposition efficiency, low coating dilution, low cost and other advantages. However, the prepared high-entropy alloy coating still has some defects and inclusions, which affect the quality and performance of the coating. This is caused by layered structure of formed coating due to the accumulation of flat particles which make difficult to maintain a high bonding rate at the interface between the particle layers. In results, a large number of unbounded areas appear at the coating which eventually becomes an internal defect. In addition, during spraying process molten particles easily react with the gas from atmospheric environment and form oxide inclusions. For these defects, the following methods can be used to improve:

- a) re-melt the coating part to a liquid state, so that it diffuses and penetrates to the surroundings to eliminate internal defects [80];
- b) annealing of the coating to recover and recrystallize initial grains which leads to forming of small equiaxed grains and eliminates many unbonded areas[81];
- c) use of the hot isostatic pressing method where coating is placed in a closed environment and defects in the coating are self-healed by adding high-pressure inert gas

to the environment and heat treatment [80].

1.9.3 Cold spraying technology

The working principle of cold spraying is to use thermocouples to heat the compressed gas (H_2 , He, or N_2 , etc.) at low temperature. The preheated compressed gas carries metal or ceramic powder particles and generates supersonic airflow through the Laval nozzle with convergent-divergent geometry[82]. When the powder is completely solid and impacts the matrix material from the axial direction, the powder particles will act on the surface of the matrix through the severe plastic deformation caused by "adiabatic shear instability" through mechanical processes such as plastic rheology or under extremely high stress and strain. In order to achieve spraying powder materials, and depositing to form a coating on the surface of the substrate[83]-[84].

During the cold spraying process, the powder deposition effect is inseparable from the powder properties and spraying parameters. The main factor that affects the particle deposition efficiency is the critical velocity when the particles hit the substrate. If the impact velocity of the powder particles during spraying is less than the critical velocity, the particles will rebound and cause partial erosion; if the velocity is greater than the critical velocity, the powder particles can be effectively deposited as a coating, but if the flying velocity of the particles is too high, it will cause a strong Erosion effect[86]. Therefore, the deposition process of cold spray coating is a dynamic erosion and deposition phenomenon. When the erosion effect is greater than the deposition

effect, an effective coating cannot be formed. When the deposition effect is greater than the erosion effect, an effective coating can be formed[87].

1.10 Conclusions and main aims of thesis

The purpose of the research is to study the structure and mechanical properties of AlNiCoFeCrTiMo HEA obtained by mechanical alloying and sintering. In order to achieve this purpose, the following tasks are solved:

1. The selection and justifying alloy powder compositions applying the phase formation empirical rules to obtain solid solutions in high-entropy alloys (determination of the mixing entropy ΔS with the Boltzmann equation; mixing enthalpy ΔH ; the difference of atomic radii δ ; the valence electron concentration (VEC), and calculate the necessary batches.

2. Fabrication of the high-entropy alloy powders by mechanical alloying and study its structure and phase composition;

3. Selection the sintering method for conservation of nanostructure and phase composition in HEA after mechanical alloying; production compact samples.

4. Study the structure, phase and chemical composition, as well as mechanical properties.

5. Analyze the results of the experiment and draw conclusions.

2 EXPERIMENTAL MATERIALS AND PROCEDURES

2.1 The selection of alloy components

In this paper, the AlNiCoFeCrTiMo high-entropy alloy is selected as the research object. The chemical proportions of the constituent elements are shown in table 2.1, the basic physical properties of the original elements are shown in table 2.2, and the mixing enthalpy of the atom pair is shown in table 2.3.

Table 2.1 – Chemical composition of the constituent elements

Element	Al	Co	Fe	Cr	Mo	Ni	Ti
Content at. %	14.29	14.29	14.29	14.29	14.28	14.28	14.28

Table 2.2 – The basic physical properties of the original elements

Parameters	Element						
	Al	Co	Fe	Cr	Mo	Ni	Ti
Atomic number	13	27	26	24	42	28	22
Atomic radius, nm	0,143	0,125	0,124	0,124 9	0,139	0,124 6	0,146
Valence electron concentration (VEC), el/at	3	9	8	6	6	10	4
Electronics	1,61	1,88	1,83	1,66	2,16	1,91	1,54
Crystal structure	FCC	HCP, FCC	BCC, FCC	BCC	BCC	FCC	HCP

It can be seen from table 1.1 that the five elements of Al, Co, Fe, Ni, and Cr have similar atomic sizes, small difference in electronegativity, high concentration of valence electrons, and most of them have simple FCC and BCC crystal structures; while Al compared with other components, Ti, Mo elements have larger atomic radius, lower valence electron concentration and smaller electronegativity.

Table 2.3 – The enthalpy of mixing (bonding energy) for different atomic pairs (kJ/mol)

Element	Al	Fe	Cr	Ti	Mo	Co	Ni
Al	–	-11	-10	-30	-5	-19	-22
Fe	-11	–	-1	-17	-2	-1	-2
Cr	-10	-1	–	-7	0	-4	-7
Ti	-30	-17	-7	–	-4	-29	-35
Mo	-5	-2	0	-2	–	-5	-7
Co	-19	-1	-4	-29	-5	–	0
Ni	-22	-2	-7	-35	-7	0	–

With Eq. (1.1), the entropy ΔS_{mix} with the Boltzmann equation, mixing enthalpy ΔH_{mix} , the difference of atomic radii δ , the valence electron concentration (VEC) were calculated and listed in tab. 2.4.

Table 2.4 – The values of ΔS_{mix} , ΔH_{mix} , the difference of atomic radii δ and the valence electron concentration (VEC) for AlFeCrTiMoCoNi alloy

ΔS_{mix} , J/mol	ΔH_{mix} , KJ/mol	δ , %	VEC, el/at	Predictable phase composition
16.17	-20.37	6.86	6.57	BCC+intermetallics

It can be seen from table 2.3. that the mixing enthalpy of Fe, Co, Cr, and Ni is negative and close to 0, indicating that these elements are prone to solid solution during the alloying process. If the enthalpy of mixing between Cr and Mo atoms is 0, Cr and Mo are easily dissolved together. However, Al has a relatively negative mixing enthalpy with Ni and Ti, and it is easy to combine into intermetallic compounds.

As summarized in table 2.4, it can conclude that the AlFeCrTiMoCoNi HEA besides bcc solid solution could contain intermetallic compounds because of large negative enthalpy. However, in many cases, the parametric approaches can only predict the phases formed during MA and thermal treatment or sintering.

2.2 Preparation method for AlNiCoFeCrTiMo high entropy alloy

The preparation of the experimental samples mainly consists of two parts. The first is the preparation of AlNiCoFeCrTiMo series high-entropy alloy powders by mechanical alloying (MA) – high-energy ball milling, and the second is the preparation of bulk high-entropy alloys by spark plasma sintering (SPS) and sintering under pressure.

2.2.1 Preparation of HEA powder

The alloying elements Al, Ni, Co, Fe, Cr, Ti and Mo powders were used in the experimental study have a purity mass percentage of more than 99.7 %, and the particle size is not greater than 45 μ m (325 mesh). According to the alloy composition ratio, the alloy element powder is weighed with an electronic balance with an accuracy of 0.01 g, and the powder is poured into a special plastic tank matched with the ball mill, and then placed on the powder mixer to mix until uniform. The uniformly mixed powder is then ball milled on a Retsch PM100 planetary ball mill. The ball mill uses vacuum stainless-steel tanks and cemented carbide balls, with a ball-to-material ratio of 10:1 and a rotation speed of 500 r/min. Before starting the ball milling, vacuumize the ball milling jar, and then fill it with high-purity argon (99.99%, 0.5 MPa) as a protective atmosphere. When the milling time is 0, 0.5, 1, 10, 20, 30 h, a small amount of powder is taken out for various characterization tests. The powder taking process is carried out in a sealed glove box protected by argon to avoid oxidation and Pollution. After ball milling, the powder was taken out and placed in a vacuum drying oven to dry for 3~5 days. After the powder is dried, the alloy powder is sieved and stored in a vacuum.

2.2.2 Preparation of solid HEA

After the HEA powder was prepared, the spark plasma sintering system (FCT system KCE-FCT H-HP D 25 system, German) is used to densify and sinter the powder.

The basic principles and its operating parts (such as graphite molds and punches) of the SPS sintering system is shown in figure 2.1. The sintering mold is a high-strength graphite mould with a maximum inner diameter of $\phi 100$ mm. In order to facilitate the removal of the sintered block, a graphite paper with a thickness of approximately 0.2 mm is placed between the cavity of the mould and between the powder and the punch.

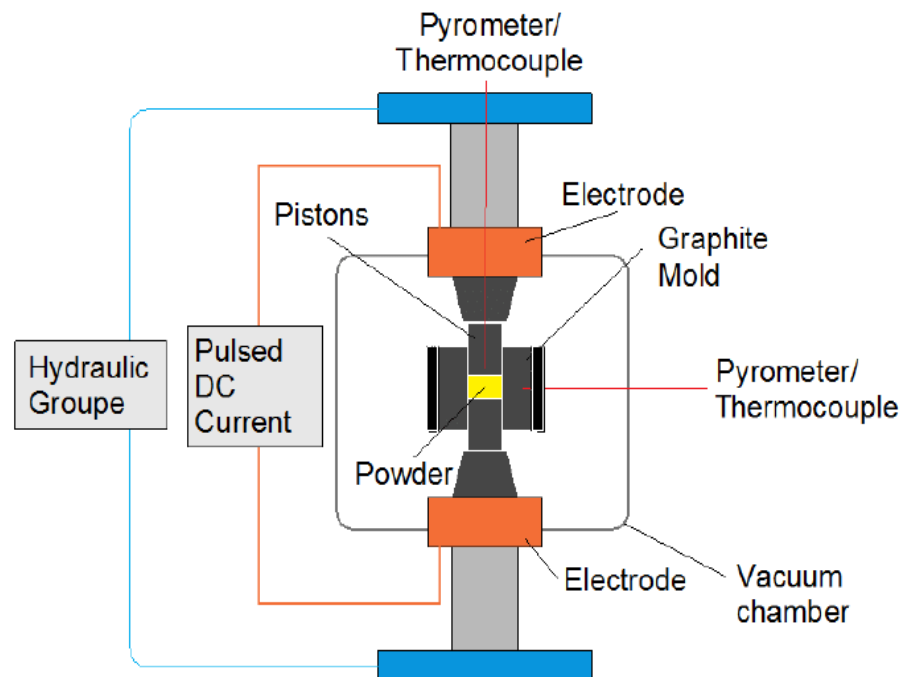


Figure 2.1 –The basic principles of the SPS and its operating parts

The basic sintering process parameters are: rise from room temperature to 900 °C in 10 minutes, then rise from 900 °C to 1000 °C in 2 minutes, and finally keep the temperature at 1000 °C for 8 minutes; the vacuum degree in the furnace is less than 8 Pa during sintering; the sintering process Maintain a constant pressure of 30 MPa during the sintering process, and cool down in the furnace after the sintering is completed. In order to compare the effects of different sintering methods on the structure and properties of

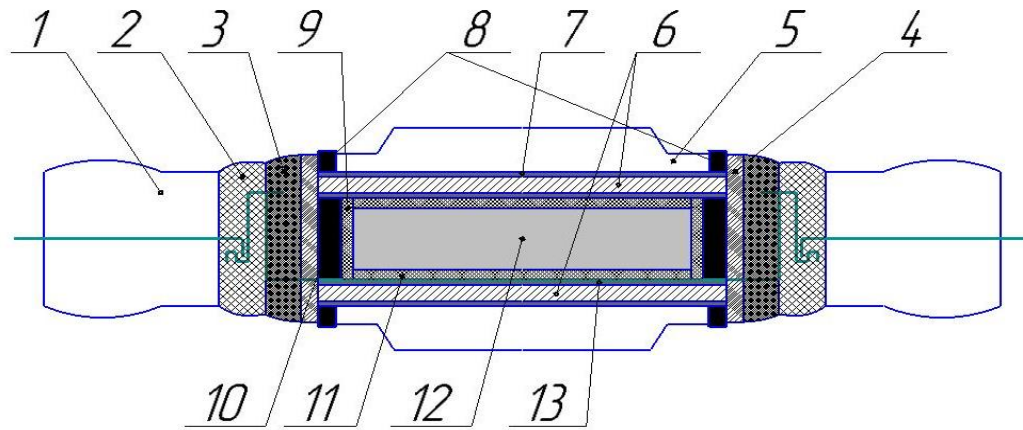
high-entropy alloys, part of the high-entropy alloy powders were sintered by vacuum hot pressing. The sintering process is as follows: in the first 40 minutes, increase from room temperature to 200 °C, then increase the temperature from 200 °C to 1000 °C in 40 minutes, and keep the temperature at 1000 °C for 60 minutes; maintain a constant pressure of 1273k during the sintering process; cool down with the furnace after sintering.

Also, the mechanically alloyed AlNiCoFeCrTiMo alloy powder was consolidated by pressure sintering at 1000 °C with 5 GPa pressure for half an hour in high purity argon atmosphere in the high-pressure apparatus DO 044 (Ryazan' High-Pressure Apparatus Factory, Russia) by using high-pressure cell in form of "toroid". Before sintering ball milled powder alloy was pressed at 300 MPa by a double-ended static pressing. Pressed samples with a size of 14 mm in diameter and 8 mm in height were obtained and placed in a high-pressure cell.

The feedstock powder is placed in a metal shell (usually carbon or stainless steel), which is degassed by vacuum and sealed. Thus prepared shell with powder is sintered at a pressure of 100-200 MPa and temperatures up to 1250-1300 °C.

The process of compaction of alloys by the SPS method, in high-pressure apparatuses, was carried out on a hydraulic press of model K 044. The cell in which sintering was carried out directly is presented in figure 2.2. This cell housed a press obtained by static double-sided pressing at a pressing pressure of 300 MPa, with a size of 14 mm in diameter and 8 mm in height. Before the sintering process, the cell was subjected to two-way compression to a pressure of 5 GPa, which was maintained throughout the sintering process. Using resistive heating, the sample was heated to a

temperature of 800 °C for 5 minutes. The sintering process lasted 30 minutes, after which it was cooled to 80 °C for 5 minutes.



1 – toroidal ring; 2 – outer sleeve; 3 - inner sleeve; 4 - tubular thermal insulator; 5 - disk thermal insulator; 6 - composite disk heater; 7 - graphite disk heater; 8 - current supply ring; 9 - heat-conducting sleeve; 10 - tubular graphite heater; 11 - heat-conducting disk; 12 - pressing; 13 - disk graphite heater

Figure 2.2 – Scheme of a mold for sintering under pressure

The sintering temperature was controlled by a thermocouple, which was fed to the heater in the form of separate parts in each layer of the cell, in order to prevent its rupture during the sealing of the cell when pressure is applied to it.

The sintered block was polished with water-resistant sandpaper with grain sizes of 180, 360, 600, 800, 1000, 1200, 1500, and 2000 in sequence, and then polished with a 1 µm diamond abrasive. The surface of the polished alloy block was corroded with self-made dilute aqua regia to obtain a suitable metallographic sample.

2.3 Characterization of microstructure and phase composition

2.3.1 X-ray diffraction analysis (XRD)

Phase analysis is performed on the alloy powder after ball milling and the bulk AlNiCoFeCrTiMo alloy after SPS densification. The instrument used is X-ray diffractometer (XRD, Ultima IV, F. Rigaku, Japan), and the scanning range is 20°-120° between. The instrument uses Cu target K α rays, the scanning step is 0.04°, and the angular velocity of the goniometer is 2 °/min.

The type of the crystal lattice of the solid solution was calculated in accordance with the ratio given by:

$$Q = \frac{\sin^2 \theta_i}{\sin^2 \theta_1} = \frac{(h_i^2 + k_i^2 + l_i^2)}{(h_1^2 + k_1^2 + l_1^2)}, \quad (2.1)$$

where θ_1 and θ_i are the diffraction angles of the first line and the i-th line respectively;

(h, k, l) is the interference index of each line in the diffraction pattern (Miller indices).

The lattice parameters of solid solutions were calculated from the position of the largest diffraction maxima gravity center at the largest diffraction angle by traditional methods using the Wolf-Bragg equation:

$$a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}, \quad (2.2)$$

where λ is the wavelength of the characteristic spectrum (Cu-1.5418 Å);

θ - the diffraction angle;

(h,k,l) – the interference index of each line of the diffraction pattern.

2.3.2 Scanning electron microscope

Scanning electron microscope (SEM, REMMA-106I) was used to observe the microstructure and morphology of the raw metal powders and high-entropy alloy block and analyze the EDS energy spectrum.

2.3.3 Thermal analysis

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the heat flowing into or out of the sample is measured as a function of temperature or time while the sample is exposed to a controlled temperature program. It is a very powerful technique that can be used to evaluate material properties such as glass transition temperature, melting, crystallization, specific heat capacity, curing process, purity, oxidation behavior, and thermal stability. DSC was used to analyze the high-entropy alloy powder after mechanical alloying for 30 hours, and analyse the thermal stability of the HEA powder.

The thermal analysis in the temperature range of 30 – 1430 °C was carried out in a STA 449 F1 Jupiter (NETZCH Germany) differential scanning calorimeter (DSC) at a heating rate of 20 K/min under flowing purified argon atmosphere. Thermal effects during heating in the temperature range of 30 – 1430 °C were recorded and compared

with the weight change of samples. The heating rate was 20 °/min. The DSC method was carried out by the simultaneous heating of two calorimetric cells (working and standard) in a constant stream of high purity Ar at a rate of 40 ml/min. Measurement and data processing were carried out in accordance with the method described in [88].

2.3.4 Vickers hardness

According to the standard method, the microhardness of HV powder is measured by Vickers method on the LHVS-1000Z instrument. The Vickers microhardness is calculated as the ratio of the applied load to the surface area of the impression:

$$HV = \frac{2F \sin \gamma_1}{d^2} \cdot 10^{-3} = 1,8544 \cdot \frac{F}{d^2} \cdot 10^{-3}, \quad (2.3)$$

where $2\gamma_1$ is the angle between the opposite faces of the Vickers pyramid ($2\gamma_1=136^\circ \pm 0.5^\circ$);

F – the force (load) exerted on the indenter during the test, the unit is H or kg;

d – the length of the diagonal, the unit is mm, d_{1-2} is the arithmetic average of the two diagonal lengths of the indenter, d_1 and d_2 .

The standard deviation of the random error of the hardness measurement result is determined by the following formula:

$$\pm \sigma = \sqrt{\frac{\sum (HV_c - HV_n)^2}{(n-1)}}, \quad (2.4)$$

where HV_c – the arithmetic mean of the hardness;

HV_n – the hardness value of the n -th measurement;

N – the number of measurements.

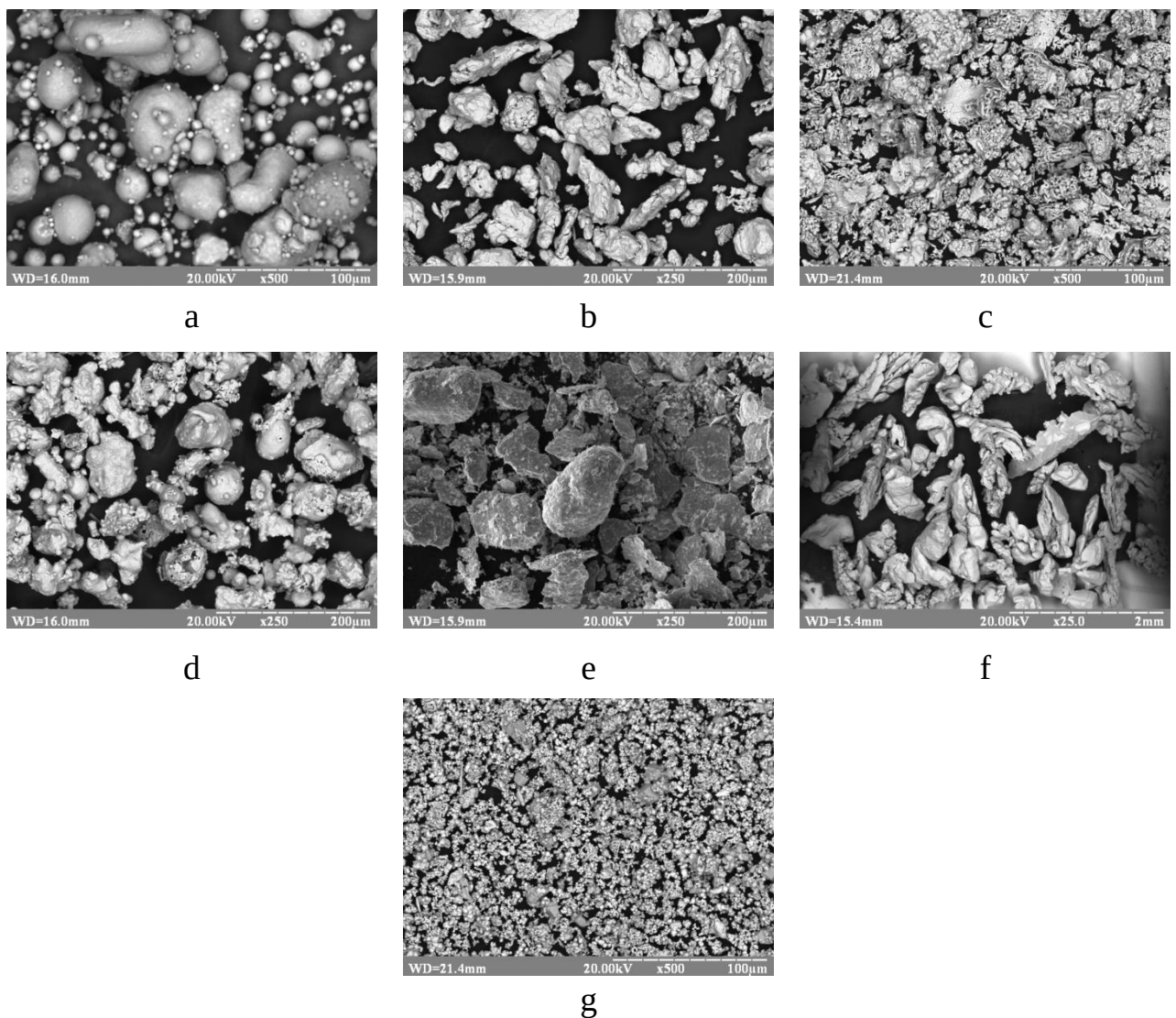
2.3.5 Mechanical testing

The mechanical characteristics of the alloys (hardness H_{IT} , elastic modulus E , and indentation elastic strain ε_{es} and associated yield stress σ_{es}) were determined by continuous indentation (Berkovich diamond pyramid) using a Micron-Gamma machine (National Aviation University, Aerospace Institute, Ukraine) in accordance with the procedure described in [90]. The load F was 1.5 N. Automatic loading–unloading lasted 30 sec, load applied to the indenter (F) and depth of indenter penetration (h) into the test material being recorded in the process. The loading, holding, and unloading F – h curve was being plotted in parallel. The load F was determined with an accuracy of 10^{-3} N and indenter penetration depth h with an accuracy of ± 2.5 nm [91].

3 RESULTS AND DISCUSSIONS

3.1 Formation of structure and phase composition of equiatomic AlNiCoFeCrTiMo high- alloy during mechanical doping

Figure 3.1 shows SEM images of morphology of powders of the initial components of the AlNiCoFeCrTiMo HEA.



a - Al; b - Ni; c - Co; d - Fe; e - Cr; f - Ti; g - Mo

Figure 3.1 – SEM images of morphology of source powder components

It can be seen from Figure 3.2 that before the mechanical alloying starts, that is, when the milling time is 0 h, the diffraction peaks of each element can be clearly detected in the mixed powder. With the increase of the milling time, the diffraction peak of Al and Co are quickly decreasing and finally disappear. After 1h of ball milling, the diffraction peak corresponding to Al element basically disappeared, indicating that Al alloyed first. When the milling time is 10h, only the diffraction peak of Mo element can be clearly detected. The disappearance of the remaining diffraction peaks means the formation of solid solution, that is, the beginning of alloying. As the milling time increases, the detected alloy element peaks become less and less, the intensity of the diffraction peaks gradually decreases, and the width gradually increases. After 20 hours of ball milling, the diffraction peaks of the mixed powder showed that a single-phase BCC solid solution had been formed, and the mechanical alloying process was basically completed. In order to make the generated BCC phase more stable and at the same time to make the alloying process more sufficient, the ball milling process was extended to 30 h, at which time the grain size has been refined to the nanometer level.

When the ball milling to 30 h, the crystal grains are fully refined, the powder size is reduced and relatively uniform, the high-entropy alloy powder is completely alloyed to form a solid solution with a simple BCC crystal structure, and a small amount of WC is also detected. The reason is the pollution caused by the cemented carbide balls and chambers during the milling process. In addition, after 30 hours MA, one more phase was formed - titanium carbide, and the spectrum shows weak and diffuse lines of TiC phase. The TiC phase could have been formed during MA process as a result of the

reaction of residual Ti, which did not dissolve in the BCC solid solution during MA, with gasoline.

It can also be seen from Figure 3.2 that during the entire mechanical alloying process, the diffraction peaks of Al, Co and Ni disappeared first, indicating that these three elements were the first to complete the alloying. The alloying sequence is most related to the melting point of the elements. The lower the melting point of the element, the easier it is to alloy; and when the melting point of the element is close, the hard and brittle alloying elements are preferentially alloyed [92]. In AlNiCoFeCrTiMo alloy, by observing the order of disappearance of diffraction peaks, it can be known that during ball milling of AlNiCoFeCrTiMo high-entropy alloy in gasoline medium, the order of alloying is $\text{Al} \rightarrow \text{Co} \rightarrow \text{Ni} \rightarrow \text{Fe} \rightarrow \text{Ti} \rightarrow \text{Cr} \rightarrow \text{Mo}$.

In addition, the interaction between different elements also has a certain effect on the diffusion rate. Negative mixing enthalpy is beneficial to increase the diffusion rate and promote the progress of alloying. Table 2.4 shows the mixing enthalpy of the AlNiCoFeCrTiMo alloys atoms, as can be seen from the data in the table, the mixing enthalpy of each pair of atoms is negative. As the milling time increases, the crystal grains continue to refine, and the enthalpy stored at the grain boundary increases, thereby further accelerating the process of diffusion and alloying. The reason why the mechanical alloying AlNiCoFeCrTiMo high-entropy alloy forms a simple solid solution structure, in addition to its high entropy effect, also benefits from the expansion of solid solubility caused by mechanical alloying. During the ball milling process, the grain sizes of the elemental components decrease down to nanometer scale. As the grain size of each principal element continues decreasing, the grain boundary volume fraction continues to

increase, alloying begins to occur, and a large amount of enthalpy change is stored in the grain boundary region and this part of the energy serves as the driving force for the formation of solid solution [93]. With the continuous extension of the milling time, the inter-diffusion between the components also continues to increase, which promotes the expansion of the solid solubility until the formation of a supersaturated solid solution in the alloy.

3.2 Thermal stability of AlNiCoFeCrTiMo alloy obtained by mechanical alloying

The interpretation of the DSC results was carried out taking into account the results of the X-ray phase analysis of samples following annealing at different temperatures (fig. 3.3).

The endothermic peak about 100 °C on the DSC curve was observed, which is associated with the evaporation of the adsorbed substances and can be related to the evaporation of process controlling agent (PCA). The wide exothermic effect in the temperature range of 130 °C to 400 °C in the DTA curve is associated with the reorganization of the dislocation structure, the relaxation of internal micro-stresses, such as structural deformation, lattice strain, etc, arising of MA process, as well as the increase of the crystallite size[94]-[97]. The exothermic 480 °C is related to the energy release during the phase transformation process. The exothermic effect at approximately 500 °C designates the dissipation of energy during phase transformation of bcc solid solution and formation of bcc and fcc solid solutions (separation of the α -phase), which is agreed with

the results of the X-ray diffraction analysis of the annealed samples (fig. 3.4). The horizontal part of the DTA curve appearing at 650 °C remains at a temperature of 840 °C, and denotes the growth of grains. After further heating, a long endothermic line on the DSC curve can be ascribed to the gradual destruction of crystalline structure under high temperature up to melting of the alloy's phases. The strongest endothermic peak, which appears at 1271 °C in this curve, corresponds to the melting point of the alloy, and its starting temperature corresponds to the solidus temperature of the alloy.

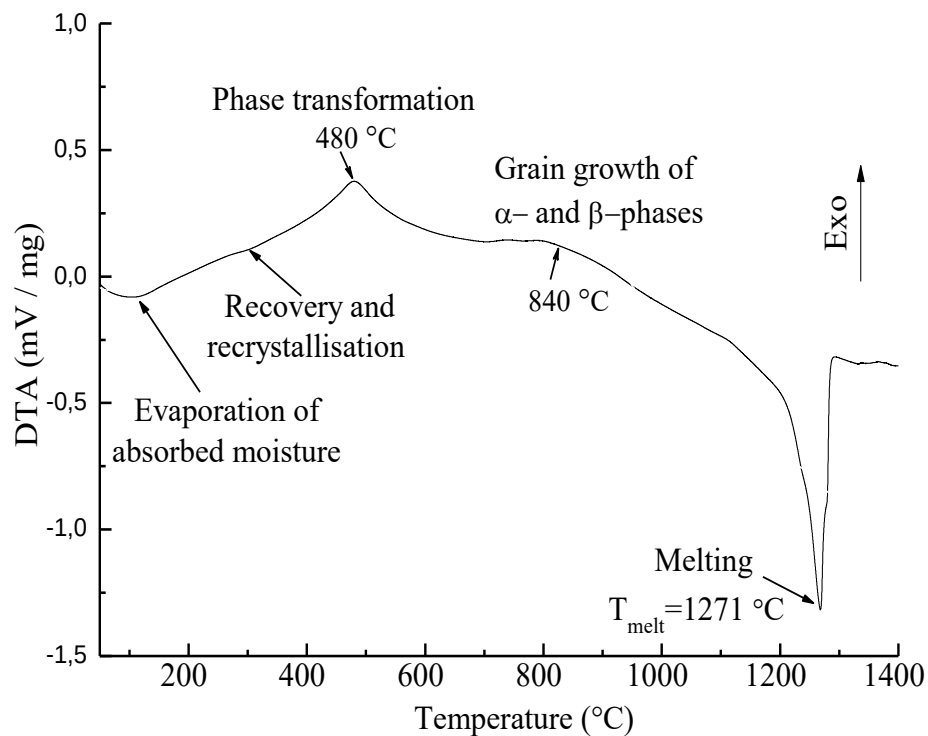


Figure 3.3 – DSC curve of the 30 h mechanically alloyed AlCuNiFeTi high-entropy alloy powder

In order to further analyze the influence of sintering temperature on the phase formation and properties of AlNiCoFeCrTiMo alloy, this article put the alloy in gasoline atmosphere and sintered at 500, 600, 700, 800, 900, and 1000 °C respectively to further

study the structure and properties. At these temperatures (500, 600, 700, 800, 900, and 1000 °C) the alloy was annealed, and after each annealing temperature the XRD analysis of the alloy was carried out as discussed below.

Effect of different temperature (500-1000 °C) under annealing on the structure and phase composition of AlNiCoFeCrTiMo alloy obtained by mechanical alloying in a gasoline environment is shown in figure 3.4.

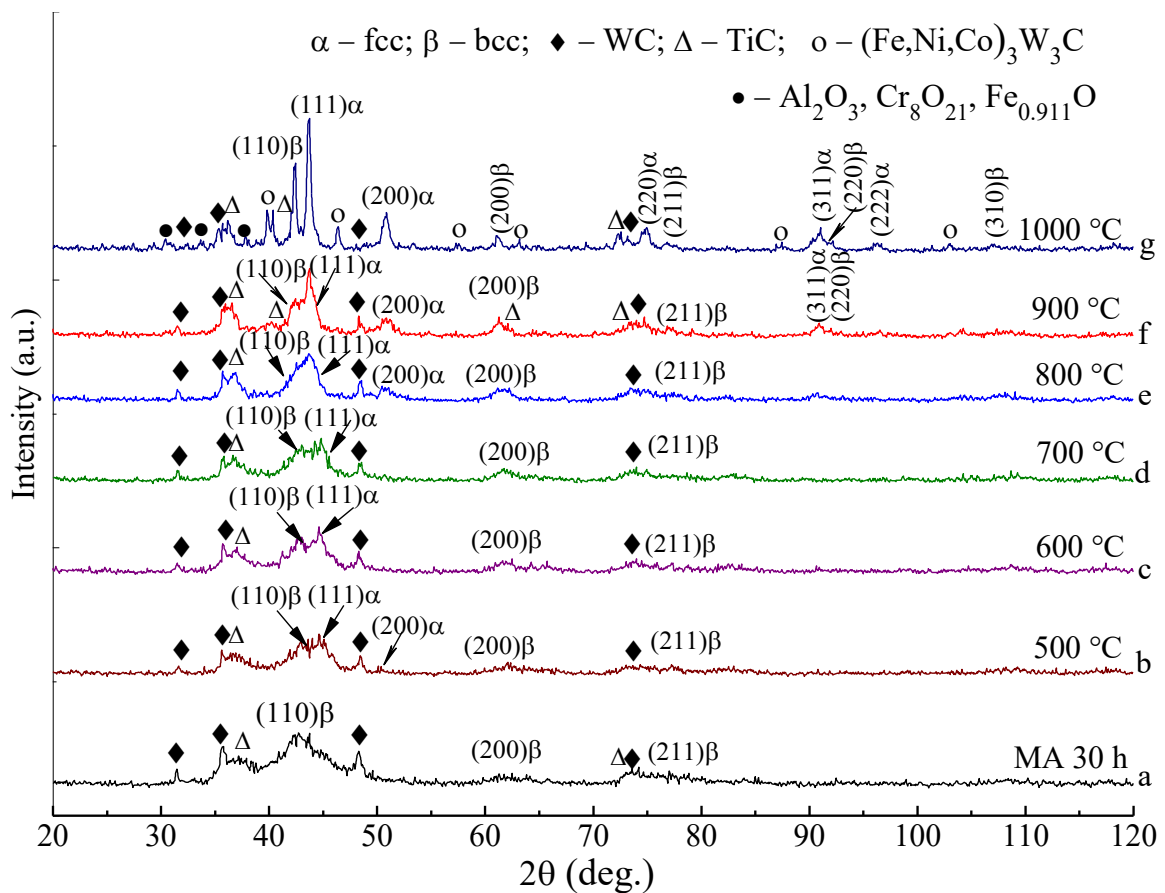


Figure 3.4 – XRD patterns of 30 h mechanically alloyed AlNiCoFeCrTiMo HEA powder after thermal annealing at different temperatures

After annealing at 500 °C, the bcc solid solution is transformed into two solid solutions (BCC→BCC+FCC). As a result, new peaks for the bcc and fcc solid solution

(β - and α -phases) were found in the X-ray diffraction spectrum (fig. 3.4 b). However, due to the low FCC solid solution content, the peaks are still very broadened and overlapped.

A further increase in the annealing temperature to 600–900 °C does not lead to significant changes in the phase composition of AlNiCoFeCrTiMo HEA, except for a gradual decrease in the width of the diffraction peaks of all phases, which become more noticeable with increasing temperature (fig. 3.4 c-f). Annealing at a temperature of 1000 °C leads to some changes in the phase composition of the alloy. In addition to the lines of BCC and FCC solid solutions, as well as TiC, weak peaks of complex carbide (Fe,Ni,Co)₃W₃C and hardly noticeable lines of aluminium, chromium, and iron oxides appear in the X-ray spectrum. The width of β and α lines of BCC and FCC solid solutions significantly decrease, while their intensity increases and they are become sharp and completely separated from one another. The Fe₃W₃C (Co₄W₂C) phase could have been formed during heat treatment as a result of the reaction of the metals of HEA with WC, which is confirmed by a decrease in the intensity of the tungsten carbide maxima (fig. 3.4).

Compared with the XRD diffraction results of AlNiCoFeCrTiMo alloy powder after 30 hours of mechanical alloying, some new phases appeared in the annealed samples after sintering into FCC phase.

The phase transformation of AlNiCoFeCrTiMo alloy after annealing at 900 °C) is affected by many factors. First, the mechanical alloying method is to prepare the alloy powder under non-equilibrium conditions, which can make the metastable supersaturated solid solution form in the alloy; secondly, the mechanical alloying makes the AlNiCoFeCrTiMo alloy form a large number of nanocrystalline grains, so the grain

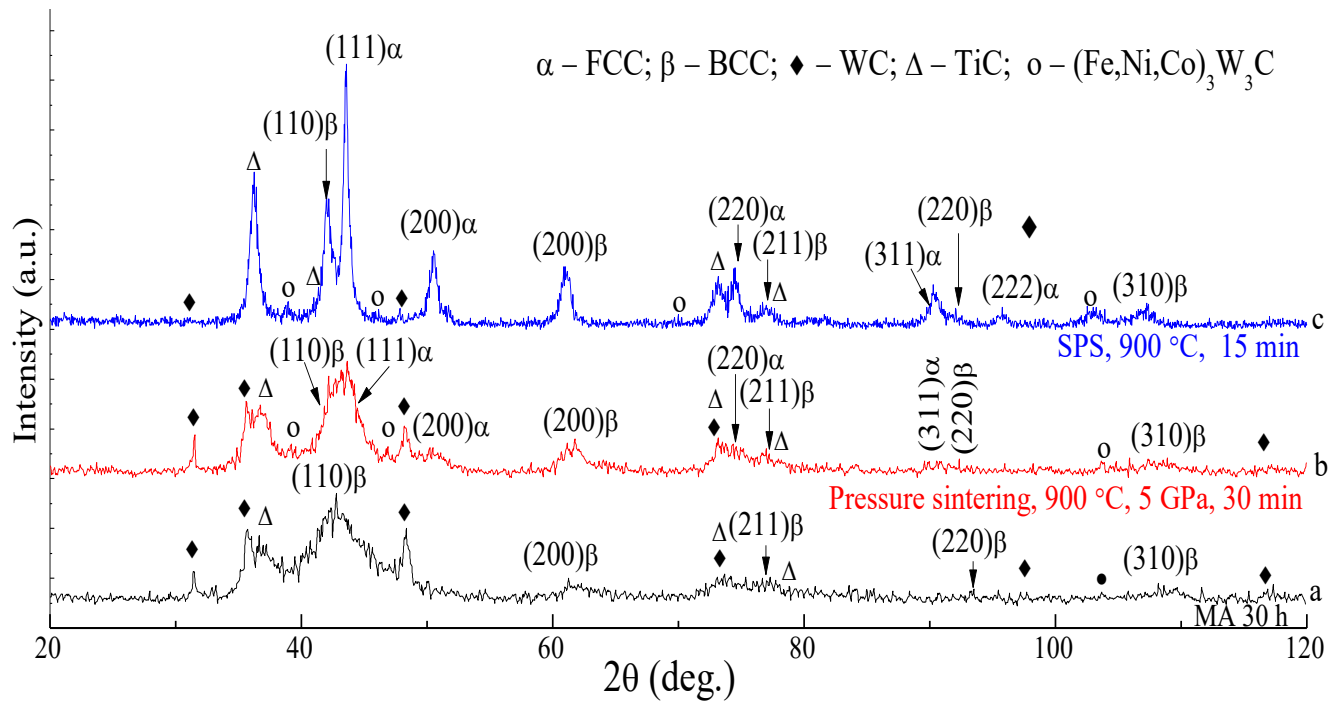
boundaries and the volume fraction are greatly increased, and a large amount of lattice distortion energy is stored at the grain boundary. The excess lattice distortion energy can reduce the activation energy required for phase transition, can effectively promote the reorganization of the crystal lattice, and provide a drive for the occurrence of phase transition. Finally, during the annealing process at 1000 °C, with the disappearance of the dislocations in the metastable phase, lattice reorganization occurs in the alloy, and the pulse current produces multi-field effects between the powders (including electric field, magnetic field, plasma Body field and temperature field). Under the superimposed influence of these factors, it may promote the occurrence of phase change.

When the sintering temperature is low, the density of the alloy is low, and there are microscopic pores. Properly increasing the sintering temperature is conducive to the densification of the alloy, and the strength, plasticity, and hardness of the alloy are improved. In the AlNiCoFeCrTiMo alloy sintered at 900 °C, lattice reorganization occurs during the sintering process, and part of the metastable due to mechanical alloying The BCC solid solution disappears and transforms into a more stable BCC and FCC solid solutions during the sintering process, which has better comprehensive mechanical properties.

3.3 Structure and phase composition of AlNiCoFeCrTiMo alloy after sintering

In order to determine the optimal sintering method for the AlNiCoFeCrTiMo HEA obtained by MA, the powder samples were sintered by SPS and under pressure 5 GPa at 900 °C and then studied.

Figure 3.5 shows that in compared with the single BCC nanocrystalline structure of AlNiCoFeCrTiMo HEA obtained after 30 hours of mechanical alloying, the AlNiCoFeCrTiMo HEA after 30 minutes of pressure sintering, and after 15 minutes of spark-plasma sintering (SPS) produces BCC and FCC phase.



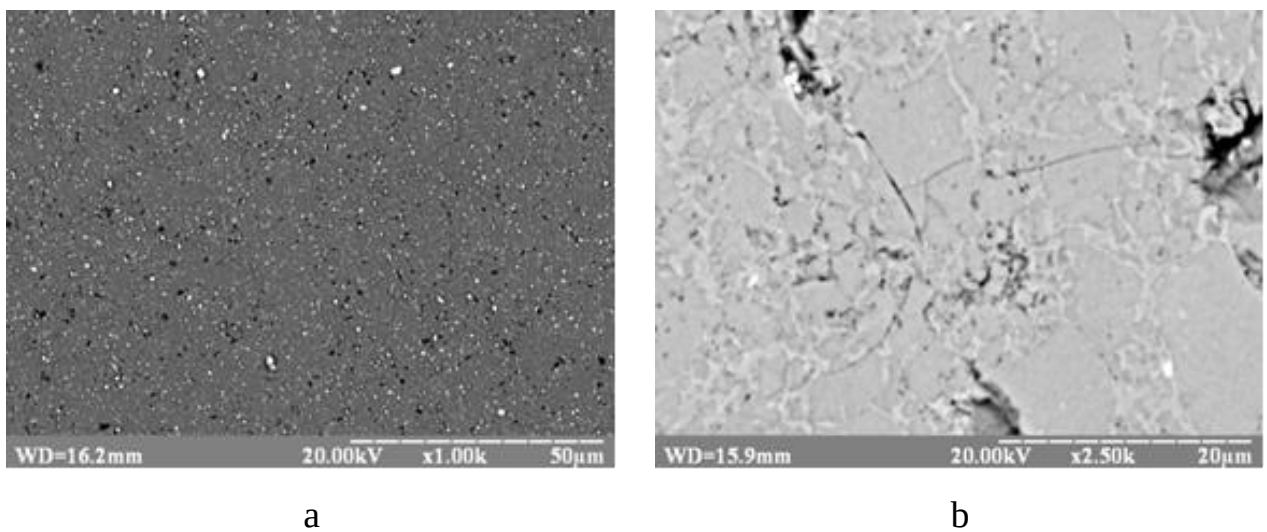
a – MA30 h; b – sintering under pressure; spark plasma sintering

Figure 3.5 – XRD patterns of the AlNiCoFeCrTiMo alloy after mechanical alloying and sintering at different modes

Compared with SPS treatment, sintering under pressure retains more BCC phase. The main reason is that during the pressure sintering process, the alloy powder is subjected to the combined effect of temperature field and pressure field; while in the process of spark plasma sintering, in addition to temperature field, pressure field, and multi-field coupling formed by electric field, magnetic field, plasma field, etc. In addition,

a remarkable feature of SPS is that it can be sintered at low temperatures. Therefore, at the same 900 °C, the use of SPS will have higher energy than hot press sintering, which makes the diffusion of atoms easier. Therefore, SPS sintering is easier to stimulate the reorganization and phase transformation of the crystal lattice in the high-entropy alloy.

Interfusion behaviour of mechanical alloying and sintering AlNiCoFeCrTiMo HEA is shown in figure 3.6.



a – sintering under pressure 5 GPa, 30 min; b – spark plasma sintering, 15min

Figure 3.6– SEM microstructure of AlNiCoFeCrTiMo HEA after sintering at 900 °C

Figure 3.6 shows the SEM image of AlNiCoFeCrTiMo HEA at 1273 K pressure sintering and sintering. It can be seen from figure 3.6 (a) that the morphology of the AlNiCoFeCrTiMo alloy after pressure sintering is mainly a dark gray area, and some black and bright white dots are scattered on the dark gray area, and the surface morphology is relatively flat and regular. And no obvious pores were found, indicating that the area has good compactness and high corrosion resistance.

It can be seen from figure 3.6(b) that the morphology of the AlNiCoFeCrTiMo alloy after sintering is a grey-white area, in which some black dots are scattered, and cracks and larger pores are generated at the same time.

These obvious surface morphologies changes should be due to the phase transformation of the BCC phase in the alloy powder during the sintering process; in addition, a small amount of bright white dots and microscopic pores can be observed, which also explains from another perspective that through the SPS sintering process. Also, it is easier to stimulate the reorganization and phase transformation of the crystal lattice in the high-entropy alloy.

3.4 Mechanical properties of AlNiCoFeCrTiMo HEA after pressure sintering

Mechanical properties of AlNiCoFeCrTiMo HEA after pressure sintering at 900 °C for 30 min at a pressure of 5 GPa are shown in table 3.5.

By comparing the various mechanical properties (Vickers hardness, microhardness) of AlNiCoFeCrTiMo alloy with AlFeCrCoCu alloy, AlFeCrCoCuMo alloy and AlFeCrCoCuTi alloy, it can be seen that the overall performance of AlNiCoFeCrTiMo alloy is better than other high-entropy alloys.

At the same time, introducing slightly lower density Cr, Ti, and Al elements into the high-entropy alloy formed by the metallic Mo alloy can significantly increase the hardness and yield strength of the high-entropy alloy, and improve the toughness and ductility of the alloy.

Table 3.5 – Mechanical Properties of AlNiCoFeCrTiMo HEA sintered under pressure 5 GPa at 1273 K for 30 min

	AlNiCoFe CrTiMo	AlFeCrCoCu [98]	AlFeCrCoCuMo [98]	AlFeCrCoCuTi [98]
Vickers hardness, (GPa)	14 GPa	4.52	5.18	5.7
Microhardne ss H_{IT}	14,6 GPa	5.93	6.58	6.45
Elastic modulus E (GPa)	157	-	-	-
Yield stress σ_{es} (GPa)	3.87	-	-	-
Elastic strain ε_{es} (%)	2.75	-	-	-

4 LABOR PROTECTION SECTION

The laboratory is an important place for teaching and scientific research. Safety work is one of the basic management tasks of the laboratory. In order to maintain the personal safety of laboratory staff, ensure that the national property is protected from loss and the normal progress of teaching and scientific research, it is very important to quickly make appropriate response measures in emergency situations, to do labor protection and to conduct tests in accordance with safety requirements. necessary.

Taking into account the possible emergencies during the test, in this part of the master's thesis, labor protection will be described from the aspects of mechanical alloying, spraying, and heat treatment.

4.1. Analysis of harmful and dangerous production factors

In the grinding process of planetary ball mill, we always think that the processed material is stable, non-flammable and explosive, and it is very safe. In fact, in the usual safe and stable materials such as iron, copper, zirconium, etc., when these materials are ground to micron or nanometer size, the activity and surface free energy will be greatly improved, resulting in more active physical and chemical properties. Of course, is also more flammable.

Another feature of ultra-fine powder materials is that the adsorption capacity is enhanced, and its contact with oxygen molecules in the air increases, and the thermal conductivity of the powder becomes weaker. All of the above will cause the material to

be more prone to spontaneous combustion and explosion hazards.

To prevent the above dangerous situation from happening, the simple way is to use wet grinding. Wet milling not only speeds up the heat transfer, but also reduces the contact between the material and the air, so that combustion and explosion will not occur. During the test, the ball milling in a gasoline atmosphere was chosen. In addition, vacuum mills and atmosphere protection mills are also a good way. Without oxygen, all burning situations will not occur, but you must be extra careful when opening the lid of the ball mill tank. Dangerous situations may occur at the moment of contact with oxygen.

The plasma surface treatment machine will produce a trace amount of ozone when it is turned on. A small amount of ozone is basically harmless to the human body, and it can effectively decompose and sterilize harmful bacteria in the air. However, if the use environment is relatively closed and the ventilation is poor, the concentration will be too high, causing people around to smell irritating odors, resulting in a slight dizziness and headache. Therefore, the plasma machine production workshop needs to be kept open to the outside air. If the use space is relatively closed and the ventilation is poor, a special exhaust system needs to be installed.

Generally, plasma spraying will be accompanied by some dangerous production consequences, such as: increased dust and gas in the work area, visible light and infrared radiation; ionizing radiation; noise, etc. Workers may be exposed to many harmful substances (dust, aerosol) during the test, these substances exist in various metals (manganese, chromium, nickel, copper, titanium, aluminum, iron, tungsten, etc.), and toxic gases (carbon monoxide), Nitrogen oxides, ozone, fluoride) hydrogen, silicon tetrafluoride, etc. The quantity, composition and toxicity of these substances depend on

the type of process and the chemical composition of the materials used.

During the spraying process, the glow beam generated by the plasma surface treatment machine will cause burns to the human body if it comes in close contact. Therefore, when the plasma beam is processing the material, it must not be touched by hand. In addition, if the eyes are not protected, it may cause damage to the visual organs (eyes, cataracts, etc.). Generally speaking, the direct-jet plasma surface treatment machine is 50mm away from the nozzle, and the rotating plasma surface treatment machine is 30mm away from the nozzle as a safe distance. At the same time, in order to operate the equipment safely, it is necessary to use AC220Vac ($\pm 10\%$) power supply and effective grounding to keep the air supply source dry and clean.

4.2 Engineering solutions to ensure occupational safety

4.2.1 Requirements for production facilities

According to the standard of ДCH 3.3.6.042-99[99], the test process is mostly standing, walking, moving small (up to 10 kg) loads and moderate physical exertion, which belong to moderate-intensity physical labor (IIb).

Plasma spraying of metals must be carried out in accordance with the requirements of the HIIAOP 28.5-1.02-07[100]. To this end, separate sites or separate test areas have been assigned. The test area should be located on the leeward side of the main wind direction relative to the residential building, and be constructed of refractory materials, located in a single-storey house with glass windows and light-transmitting lights, and keep a certain distance (not less than 50 m) from the residential building to facilitate

spreading harmful materials. The plasma spraying machine must be protected by a fixed device, or a portable opaque fence made of non-combustible materials, and the height of the fence must be at least 2.5 m and ensure the reliability of the protection.

The plasma spraying of metal should be carried out in a controlled closed room, and the auxiliary operations of plasma spraying (processing, cleaning, powder preparation, etc.) should be carried out outside the main area. When plasma technology is used, the local exhaust device should use technology to block the equipment. Manual plasma spraying must be carried out in a sheltered exhaust cabinet, and its inner surface must have a sound-absorbing coating. The compressed gas cylinder must be installed outside the plasma zone, and then the gas is supplied to the intake hood for processing.

In order to eliminate the possibility of electric shock and generally for electrical safety, it is necessary to check the operation of the remote control button device. Turn the equipment on and off to prevent accidental startup of the equipment and provide blocking equipment that automatically cuts off the power in the event. All plasma spraying operations must be attended by at least two workers at the same time. The distance between the equipment, from the equipment to the walls and pillars of the room, the width of other structures, passages and passages must comply with the current building codes, store technical design codes and ДБН В.2.5-67:2010[101]. The aisle width around the desk, stand, and work product must be at least 1 m.

4.2.2 Requirements for production buildings and sites

Floors of industrial sites used for plasma spraying operations must be made of non-

combustible materials with low thermal conductivity. The ground must have a smooth non-slip surface and meet sanitation and hygiene requirements. Production facilities must be equipped with universal switching power supply exhaust ventilation in accordance with DBN B.2.5-67: 2013[102].

The height of the shop depends on the number of available spans, dimensions of the equipment used and machined parts and must be at least 8 m. The height of the entrance gate of the shop must be at least 5.4 m, width - at least 4.8 m (for rail transport). The shop must have at least two evacuation exits. The door must be at least 0.8 m wide and at least 2.0 m high.

4.2.3 Ventilation requirements

The amount of air discharged or supplied by the ventilation device (the amount of air exchange required by the production site, L , in m^3/h) is determined by different methods according to specific conditions: gas, according to the empirical formula or the recommended air exchange amount. In the case of data on the intensity of the release of harmful substances into the atmosphere. In general, the indoor air exchange rate is calculated according to the following formula:

$$L = \frac{1000\beta V}{C_{\text{гдк}} - C_{\text{пр}}}. \quad (4.1)$$

In the formula, V is the intensity of harmful substances released per unit time, g/h ;

β - the coefficient of uneven distribution of harmful substances in the room volume;

$C_{ГДК}$, $C_{пп}$ -the concentration of harmful substances in the air discharged (exhausted) and entered (inflow), mg /m³.

If the air in the work area is removed and $C_{пп} = 0$,

$$L = \frac{1000\beta V}{C_{ГДК}} \quad (4.2)$$

If it comes from the upper area, then

$$L = \frac{1000\beta V}{K_{п}C_{ГДК}} \quad (4.3)$$

Where $K_{п}$ - air exchange coefficient (has a value of 0.9 ... 1.1 when supplying air with horizontal jets; 1.65 ... 1.85 – when supplying to the working area; 1.25 ... 1.4 at a height of 4 m).

The maximum allowable concentration of aluminum and alloys in the air is 2 mg/m³, substituting into the formula to calculate:

when supplying air with horizontal jets,

$$L = \frac{1000\beta V}{K_{п}C_{ГДК}} = 35.20 \text{ m}^3/\text{h} \quad (4.4)$$

when supplying to the working area,

$$L = \frac{1000\beta V}{K_{\Pi}C_{ГДК}} = 20.11 \text{ m}^3/\text{h} \quad (4.5)$$

The calculation of the amount of air discharged by local ventilation L_M is determined based on the given intake rate at the source of harmful substances, the characteristics of the intake rate spectrum of the specific intake design opening and the existence of the surface surrounding the intake area. under these circumstances,

$$L_M = 2600 \cdot F_0 V_0 = 1404 \text{ m}^3/\text{h}. \quad (4.6)$$

Where F_0 is the cross-sectional area of the suction port and exhaust port opening, m^2 ;

V_0 is the suction rate of air in the tank, m/s .

The area F_0 is determined by the design features of the process equipment and the selected exhaust device. When using arc and plasma technology. The value of V_0 is obtained based on the condition that a given air velocity V_x is provided in the arc area at a distance X (m) from the center of the suction hole.

According to the analogy between these processes and known arc welding and plasma technology processes[103], the air velocity generated by the local exhaust near the source of hazardous materials should be: not less than 1.3 m/s .

For the simplest shape of the sharp-edged exhaust device, the suction speed is calculated by the following formula:

$$V_0 = 16V_x(X/d)^2, \quad (4.7)$$

where d - the diameter of the round hole or the hydraulic diameter for the square hole, which can be conditionally equal to the square of the velocity, m.

So, the suction speed can be calculated

$$V_0 = 16V_x(X/d)^2 = 8 \text{ m/s}. \quad (4.8)$$

4.2.4 Requirement of electrical safety

In the process of using electrical appliances, the main reasons for electric shocks are:

- contact with live parts that are live in working mode or accidentally live parts;
- failure to comply with operating guidelines and failing to take safety protection measures;
- arc and step voltage, etc.

The electrical equipment used in the production process, including technology, machinery and auxiliary equipment, must meet the requirements [104]-[105]. The electrical products used in the test must meet the requirements of PUE-2017[106] in terms of safety. In their design, it can be used in operation mode:

- insulation of live parts (working, additional, double, reinforced);
- safe voltage in the circuit;

- protective covers to prevent accidental contact with live parts and moving and heated parts;
- prevent wrong actions and operations;
- components used to control insulation and signal damage to it, and components that shut down the product when the insulation resistance drops below the allowable level;
- warning inscriptions, signs, paintings of signal colors and other dangerous signal means (combined with safety measures);

4.2.5 Requirement of fire safety

According to the requirements of HAПБ Б.03.002-2007[107], plasma spraying belongs to the category of D explosion and fire hazardous places. In the part of the production workshop where plasma spraying is used, we envisage the installation of carbon dioxide fire extinguishers, excavators, crowbars, buckets, etc. Supplies. We placed boxes with sand near the test area and regularly checked the dryness of the sand. In order to extinguish possible fires, we also envisage the use of asbestos.

Fire safety is provided by:

- prevention of flash of isolation at short circuit due to the maximum jet protection;
- prevention of combustible environment formation due to reliable sealing of equipment, restriction of use and storage of combustible and explosive substances;
- application of the fire alarm system with the sensor (IDF-I, DPID, etc.);

- using fire extinguishers (fire class B): OHP-10, OHVP-10, OVP-7, OH-7, OP-10A; for fire class E fire extinguishers type UO, OP-10A (choose the type and quantity in accordance with NAPB B.03.002-2007).

When organizing the technological process, all the requirements of electrostatic intrinsic safety are observed.

Emergency draining of flammable liquids, emergency injection of flammable gases from the equipment is also envisaged.

It is recommended to periodically clean the workplace of the shop, equipment from combustible waste, dust deposition, removal of flammable production waste, replacement of LVZh and GZh with flammable technical detergents.

Devices are provided that limit the spread of fire (describe specifically).

The room is equipped with means of collective and individual protection of people from dangerous factors of fire and smoke protection.

The type of electrical equipment in the room must correspond to the class of the fire and explosion protection zone.

4.2.6 Labor protection conclusion

In summary, laboratory emergencies are caused by many unstable factors, so laboratory personnel must attach great importance to laboratory safety. Otherwise, it will cause a safety accident. In order to avoid safety accidents, we must first clarify laboratory safety guidelines, strengthen safety awareness training for test participants, and

standardize experimental operations. In addition, test equipment needs to be checked regularly to minimize the risk of emergencies.

5 ENERGETICAL SECTION

5.1 Energy for research

Costs under this article are calculated only when research on the topic is related to melting, coating samples or products, heat and chemical-thermal treatment, etc. and require significant energy costs and, above all, electricity.

In other cases, energy costs are included in the calculation of the estimated cost of the topic in proportion to the amount of labor costs of the main performers or in proportion to the amount of direct costs to perform the research topic according to the standards of the organization performing this study.

This article includes the costs associated with the management of the executing organization, the costs of invention and rationalization; depreciation costs of fixed assets; costs of scientific and technical information; costs of ensuring normal working conditions and safety; costs of paying for bank services; taxes, fees and other obligatory payments and expenses, etc.

Consider the option of calculating overhead costs in proportion to the amount of direct costs at the level of 20%.

$$H_B = (TC + SSC + B_M + I_B) \cdot 0,2 \quad (5.1)$$

Now H_B will be:

$$H_B = (21736.29 + 4781.98 + 10490.04 + 3700.83) \cdot 0,2 = 8141.83 \text{ UAH}.$$

6 ECONOMICAL SECTION

6.1 Labor costs

Labor costs are calculated based on the complexity of a single work on the subject (Tabl. 6.1) and the wages of its direct performers (Tabl. 6.2).

Table 6.1 - The complexity of work on the topic

Name of works on the research topic	Leading researcher	Senior Researcher	Research engineer	Laboratory assistant
1	2	3	4	5
1. Clarification and specification of tasks on the research topic	1	-	-	-
2. Analysis of scientific and technical publications on the topic	-	4	2	3
3. Preparation of HEA powder	-			5
4. Preparation of solid HEA	-	1		5
5. Characterization of microstructure and phase composition (XRD, SEM, thermal analysis and Vickers hardness)	1	2	3	18
Total workers of the theme	2	10	5	31

Further calculations of labor costs are carried out according to the algorithm understood from table 6.2.

The average daily wage by category of performers is calculated by dividing their monthly salary by 21.2 (where 21.2 is the average number of working days per month).

Table 6.2 - Calculation of labor costs^[1]

Position of performers of the theme	Planned labor intensity, people-days	Salary, UAH		
		Monthly salary	Average daily salary	Total for performers
1. Leading researcher	2	20 507.09	970,29	1940.58
2. Senior researcher	10	19 266.41	908,79	9087.9
3. Research engineer	5	7895	263.17	1315.83
4. Laboratory assistant	31	6245	294.58	9391.98
Total pay on the topic				21736.29

[1] Staff list of the National Technical University of Ukraine "Kyiv Polytechnic Institute named after Igor Sikorsky" [Electronic resource]: KPI site. Igor Sikorsky ». Access to the resource: <https://kpi.ua/stafflist>.

6.2 Single social contribution

The Single Social Contribution (SSC) is a mandatory deduction for national social insurance. From January 1, 2016, the SSC rate is 22%. The calculation of SSC is based on the total labor cost in the topic (summary of Table 6.2).

$$SSC=TC*0.22 \quad (6.1)$$

TC - Total labor cost for the subject

$$SSC=21736.29*0.22=4781.98 \text{ UAH} \quad (6.2)$$

6.3. Materials required for research

This article takes into account the cost of all types of materials required for research, minus the cost of returnable waste.

Topics of research work performed at the Institute of Metallurgy and Welding. EA Paton, involves the use, first of all, charge materials, technological materials for thermal, chemical-thermal treatment and application of special coatings, chemical reagents, consumables for office equipment and more.

We accept transport and procurement costs at the level of 10 % of the planned cost of total costs for materials:

$$T_B = 9536.4 \cdot 0.1 = 953.64 \text{ UAH} \quad (6.3)$$

Calculations are summarized in the form in table 6.3.

Table 6.3 - Calculations of material costs

Name of material	Standard, technical conditions	Unit	Number	Market price per unit, UAH	Amount, UAH
Aluminum powder	GOST 6058-73	kg	1	224.70	224.70
Nickel powder	GOST 9722-97	kg	1	774.00	774.00
Cobalt powder	GOST 123-2008	kg	1	2854.80	2854.80
Iron powder	GOST 13610-79	kg	1	549.00	549.00
Chromium powder	GOST 14-00186482-051-2005	kg	1	375.90	375.90
Titanium powder	GOST 14-22-57-92	kg	1	1800.00	1800.00
Molybdenum	GOST 48-19-316-80	kg	1	2958.00	2958.00
Total cost of materials					9536.40

In this case, the total cost of purchasing materials and transporting them will be:

$$B_M = 9536.4 + 953.64 = 10490.04 \text{ UAH} \quad (6.4)$$

6.4 Other direct uncalculated costs

This article combines all the costs of SSC that are not included in the previous articles. When carrying out work, we accept other direct costs at the level of 10% of the amount of accrued costs for SSC.

$$I_B = (TC + SSC + B_M) \cdot 0,1 \quad (6.5)$$

Now I_B will be:

$$I_B = (21736.29 + 4781.98 + 10490.04) \cdot 0,1 = 3700.83 \text{ UAH}$$

6.5 Development of a planned calculation of the estimated cost of the topic

The planned calculation of the cost of research on the topic is based on the calculations and regulatory data (Tabl. 6.4).

Table 6.4 - Planned calculation of the estimated cost of research

Name of cost items	Amount, UAH	Rationale
1. Labor costs	21736.29	According to calculations
2. The only social contribution	4781.98	22.0 % of total labor costs
3. Materials for research	10490.04	According to calculations
4. Energy for research	-	According to the calculations (in our case, the article includes overhead costs)
5. Special equipment for scientific purposes	-	According to the calculations (in our case, the article includes overhead costs)
6. The cost of services of third parties	-	Under the agreement with third-party organizations (in our case, overhead costs are included in the article)
7. Expenses for business trips	-	According to the calculations (in our case not provided)
8. Other unaccounted for direct costs on the topic	3700.83	10 % of the amount of direct estimated costs on the topic
9. Overhead	8141.83	According to the standards of the organization-executor of the theme (in our case 20 % of the amount of direct costs)
10. Total costs on the topic	48850.97	The sum of previous articles

6.6 Scientific and technical efficiency of research

The calculation of the expected economic effect of research work is necessary to determine the feasibility of this work. However, it can be calculated only for research work, which is directly aimed at creating new materials, improving product quality parameters, as well as creating new designs.

To determine the annual economic effect, we use a scoring system to assess economic efficiency on the following indicators:

- the importance of development (K_1);
- the possibility of using the results of development (K_2);
- theoretical significance and level of novelty (K_3);
- the complexity of the study (K_4).

K_1 :

The coefficient K_1 can take the following values:

- a) initiative work, which is not part of a comprehensive program and is not the task of policy makers - 1 point;
- b) work is performed under the agreement on scientific and technical cooperation - 3 points;
- c) work is part of the departmental program - 5 points;
- d) the work is part of a comprehensive interagency program with elements of implementation of results - 7 points;
- e) the work is part of an international comprehensive program - 8 points.

K_2 :

The coefficient K_2 can take the following values:

- a) the results of development can be used only in this section - 1 point;
- b) the results of development can be used only by one organization - 3 points;
- c) the results of development can be used by several organizations - 5 points.
- d) the results of development can be used on the scale of one industry - 8 points;
- e) the results of development can be used in various fields - 10 points.

K_3 :

The coefficient K_3 can take the following values:

- a) the work is an analysis, generalization or classification of known information, similar results were previously known in the study area - 2 points;
- b) during the work received new information that complements the idea of the essence of the studied processes - 3 points;
- c) as a result of the work received new information, which partially changes the perception of the nature of the studied processes - 5 points;
- d) as a result of research, new theories, methods, etc. were created - 6 points;
- e) the received information forms essentially new representations which were not known earlier - 8 points.

K_4 :

The coefficient K_4 can take the following values:

- a) the work is performed by one unit, costs up to 10,000 hryvnias - 1 point;
- b) the work is performed by one unit, costs from 10,000 to 50,000 hryvnias - 3 points;

c) the work is performed by one unit, costs from 50,000 to 100,000 hryvnias - 5 points;

d) the work is performed by several departments, costs from 100,000 to 200,000 hryvnias - 7 points;

e) work is performed by several organizations, costs over 200,000 hryvnias - 9 points.

Through the above description, the total score (B) is calculated by multiplying the coefficients:

$$B = K_1 \cdot K_2 \cdot K_3 \cdot K_4 \quad (6.6)$$

In our case, the scoring of efficiency according to table. 6.5 is:

$$B = 3 \cdot 8 \cdot 3 \cdot 5 = 360$$

The conditional effect of GDR is calculated by the formula:

$$E_{\text{HДР}}^y = 500 \cdot B - E_{\text{H}} \cdot B_{\text{HДР}} \quad (6.7)$$

where 500 - the notional value of one point;

E_{H} - normative coefficient of economic efficiency (can be in the range of 0.1 - 0.3);

$B_{\text{HДР}}$ - total costs of SSC (summary of table. 6.4);

In our example, the conditional effect of SSC will be:

$$E_{\text{HDP}} = 500 \cdot 360 - 0,25 \cdot 48850.97 = 167787.26 \text{ UAH}$$

Table 6.5 - Score evaluation of the effectiveness of research

GDR performance evaluation indicator	Symbol of the indicator	Characteristics of this work	Scores
1. The importance of development	K_1	The work is performed under an agreement on scientific and technical cooperation	3
2. Ability to use development results	K_2	The results of the development can be used on the scale of one industry	8
3. Theoretical significance and level of novelty of development	K_3	During the work, new information was obtained, which complements the idea of the essence of the studied processes	3
4. The complexity of the study	K_4	The work is performed by several departments, costs from 50,000 to 100,000 hryvnias	5

The economic efficiency of research is determined by the coefficient of conditional economic efficiency E_e . It is the ratio of the conditional effect of SSC to the total cost of SSC and is calculated by the formula:

$$E_e = \frac{E_{\text{HDP}}}{B_{\text{HDP}}} \quad (6.8)$$

In our example E_e will be:

$$E_e = \frac{167787.26}{48850.97} = 3.43$$

The coefficient of conditional economic efficiency of research work is 3.43 (> 1), which indicates the feasibility of its implementation.

7 STARTUP SECTION

7.1 Introduction of startup

A startup is a newly created company (maybe not yet officially registered), which forms its business on the basis innovation or innovative technology, has limited number of resources (both human and financial) and plans enter the market.

Startup as a form of small risky (venture) business over the past decade has become widespread in the world due to lower barriers to market entry (with the advent of the Internet as a tool of communication and marketing has become easier to find consumers and investors, search for resources, cross borders between markets and countries), and is considered one of the cornerstones of the innovation economy, because due to mobility, flexibility and a large number of startup projects, the total mass of innovative ideas is growing.

With the advancement of science and technology and the development of society, people have higher and higher requirements for materials in industrial and living applications, and the requirements for the performance of materials in various aspects under harsh use conditions are becoming more and more stringent. At present, trillions of equipment materials and infrastructure are damaged to varying degrees every year, and the failure process mostly starts from the surface (such as surface wear, corrosion, etc.), frequent equipment maintenance and uninterrupted equipment outages. The economic loss to come is impossible to estimate.

Take the commonly used knives and scissors in daily life as an example, blade wear and corrosion are the main failure modes. Although the current tool materials have

changed from carbon steel to ordinary stainless-steel materials, and then developed until now, high-carbon and high-chromium stainless steel materials have been innovated, but they have insufficient wear and corrosion resistance during service and cannot be maintained for a long time. The sharpness and other shortcomings have always restricted the further development of domestic cutting tools. However, the use of high-entropy alloy combined with plasma spraying technology to modify the surface of the knife can greatly improve this situation.

The cutting tool is an important part of the metal cutting machine tool to realize the cutting function, and it is complementary to the machine tool system. Metal cutting is the most basic, most reliable, and most widely used precision machining method in machining. Metal cutting tools are the terminal key components directly involved in cutting in the manufacturing field. Their quality directly determines the production level of the machinery manufacturing industry and is an important factor for the manufacturing industry to improve production efficiency and product quality. Tool and machine tool are two complementary and relatively independent subsystems, which play an equally critical role in modern manufacturing.

The blade is the key element of the metal cutting tool to realize the cutting function, and it has the properties of consumables. Cutting tools include indexable tools, integral tools and welding tools. Among them, the indexable tool is composed of a blade, a cutter head/bar and a handle. The blade assumes the function of cutting and forming the surface to be processed. After the blade is worn, only the blade can be replaced without replacing the entire tool. The blade is the key consumable that realizes the function of the tool and determines the performance of the tool.

The compulsory part of the master's thesis allows to complete professional training of future experts and form their important professional skills in innovative technology and innovative technology development to verify their effectiveness and the possibility of introduction, and to ensure a competitive product at the national level And the production efficiency of services, and it is of great significance in opening up the world market and realizing the stable development of the national economy. Therefore, the relevance of the development of the startup project in the implementation of the master's thesis is beyond doubt.

High-entropy alloys have excellent properties that are unmatched by traditional alloys, such as high strength, high hardness, high wear and corrosion resistance, high thermal resistance, high resistance, etc., and become a major relay in the fields of materials science and condensed matter physics. A new research hotspot after bulk amorphous alloys. At present, there are many methods for preparing high-entropy alloys of refractory metals. Magnetron sputtering and laser cladding can prepare high-entropy alloy films and coatings. Vacuum arc furnace casting and powder metallurgy can prepare bulk materials. However, due to the high melting point of refractory metals, the size of castings is limited, and the molding of castings is difficult to guarantee. Research on it is limited to the laboratory level, and industrialized mass production cannot be realized. In addition, the casting alloy requires subsequent homogenization treatment, which results in higher production costs and lower production efficiency.

Compared with the melting and casting method, mechanical alloying (MA) is a solid non-equilibrium high-energy ball milling process, which can achieve alloying between high-entropy alloying elements with large melting points, and the mixed powder can form

metastable after mechanical alloying Phase, supersaturated solid solution, amorphous intermetallic compound. Spark plasma sintering (SPS) can quickly sinter to prepare high-entropy alloys. The sintering process can inhibit the growth of grains and obtain bulk materials with high density and uniform organization.

Compared with the melting and casting method, the method of preparing high-entropy alloys by mechanical alloying and spark plasma sintering is expected to produce high-entropy alloys with larger size, finer grains and uniform structure distribution on the premise of saving production costs.

The purpose of the section is to form innovative thinking, entrepreneurial spirit and ability to assess market prospects and opportunities for commercialization of major scientific and technical developments formed in the previous part of the master's thesis in the form of developing a startup project in a highly competitive market economy.

The task of the section is the marketing analysis of prospects for the implementation of the proposed master's scientific and technical solutions and proposals, assessing the possibilities of their market implementation.

7.2 The contents and characteristics of the startup stage

At the beginning of the development of a startup project, it is important to determine the contents and characteristics of the startup stage (Tabl. 7.1).

Table 7.1-The essence and specifics of the stage of a startup

Title	Contents	Activity	Completion
Sowing stage	Search and definition of the idea of a startup and forms of its implementation	Search for an entrepreneurial idea. Collection of initial information. Design and initial presentation of the idea. Analysis of eligible volumes and sources of funding	Entrepreneurial idea. Startup implementation plan. A management team has been formed. Project schedule. Registered organization.
Startup stage	Materialization of a business idea	Activation and use of human resources, material, technical and technical support	An existing organization that implements a startup
Growth stage	The growth of the startup company and its scaling activities	Ensuring uninterrupted and high-quality production, distribution through distribution channels and sales of products	Scaled business. Higher growth rate than average economic growth rate. Transition from investment to self-financing
Stage of expansion	Transformation of a startup company into an existing enterprise	Expansion of activity. Diversification, product improvement. Business scaling	Operating enterprise
Exit stage	Sale of a company or share of ownership	Sale of shares. Business buyout	The transition of a startup to the business sphere

At present, the research on AlNiCoFeCrTiMo high-entropy alloy is still in the exploratory stage, and it has not been widely promoted from the laboratory to the market. Although some experts and scholars have studied the element composition and content of high-entropy alloy, preparation process and microstructure and performance. But so far, a more mature theoretical system has not been formed. Therefore, it is undoubtedly of very important theoretical and practical significance to carry out relevant research work on high-entropy alloys and invest them in startup projects (Tabl. 7.2).

Table 7.2 - Description of the idea of a startup project

Content of the idea	Directions of application	Benefits for the user
The failure process of metal tools mostly starts from the surface (such as surface wear, corrosion, etc.), and the economic losses caused by frequent equipment maintenance and uninterrupted equipment outages cannot be estimated. However, the use of high-entropy alloy combined with plasma spraying technology to modify the surface of the knife and improve the strength, hardness and wear resistance of the tool can greatly improve this situation.	Production of cutting tools based on AlNiCoFeCrTiMo high-entropy alloy.	Improve the wear resistance and strength of the tool, greatly improve the efficiency of use, and extend the service life of the tool
	Production of drills based on AlNiCoFeCrTiMo high-entropy alloy.	Improve the wear resistance and strength of the tool, greatly improve the efficiency of use, and extend the service life of the tool

7.3 Analysis of the competitive environment

With the rapid and vigorous development of modern manufacturing, the complexity and difficulty of processing parts in high-end equipment manufacturing industries such as aerospace, national defense and military industry, nuclear industry, and shipbuilding are getting higher and higher, and the requirements for the performance and precision of CNC tools are also increasing. Higher and higher, high-end cutting tools have advantages in terms of structure, materials, coatings, etc., which can meet the requirements of modern manufacturing for precision machining of parts.

As competition in the cutting tool industry continues to intensify, mergers and acquisitions and capital operations among large companies are becoming more frequent. Excellent tool companies at home and abroad are paying more and more attention to the analysis and research of the industry market, especially the current market environment and changes in customer demand trends. In-depth research, with a view to occupy the market ahead of time and gain first-mover advantage. Among them, the analysis of the competitive environment in the industry is particularly important.

On the other hand, as the cutting processing technology of different end customers develops towards specialization and high efficiency, the customization and individualization requirements of cutting tools are increasing, and the cutting tool suppliers need to be based on the specific indicators of their processing environment, processing equipment and processed parts. The design of tool allocation plans, and customized production and installation, put forward higher requirements on the design

ability, response speed, customized production and service capabilities of tool manufacturers, so as to provide customized, one-stop products with high-cost performance. A comprehensive tool manufacturer with tooling solutions is in an advantageous position in the competition in the same industry. The comparative analysis of indicators is carried out: for the own idea the indicators having a) worse values (W, weak); b) similar values (N, neutral); c) the best values (S, strong). The results of the analysis are summarized in table 7.3.

Table 7.3 - Identification of strong, weak and neutral characteristics of the project idea

№	Technical and economic characteristics of the idea	(potential) products / concepts of competitors			
		My project	Competitor 1	Competitor 2	Competitor 3
1.	New technology	S	N	N	N
2.	Less consumables	S	N	W	N
3.	Excellent performance	S	W	N	N
4	Service life	S	W	W	N

At the same time, during the implementation of the startup project it is expedient to conduct a SWOT analysis of potential threats and opportunities for implementing the

startup project, identifying strengths and weaknesses, as well as its capabilities and threats (table 7.4).

Table 7.4 - Form for SWOT analysis

Factors	Assessment of the environment		Enterprise evaluation	
	Opportunities	Threats	Strengths	Weak sides
1. Dependent on the activity of the enterprise: 1.1. Technology 1.2. Material	1. The rapid development of social science and technology 2. A large number of new alloy materials have been developed	1. The rapid development of other competitors' technology 2. The growth of market sales has slowed down	1. Have the ability to resist competitors 2. High material cost	1. Complex production process 2. High material cost and insufficient profitability
2.It is independent of the activity of the enterprise: 2.1. Market	Industry demand is high, consumer coverage is wide	There may be substitutes	Have a competitive advantage	Real competitiveness is not strong

The results of the SWOT analysis should be generalized in the corresponding matrix (Tabl. 7.5).

Table 7.5 - SWOT Analysis Matrix

S (strength)	W (weaknesses)
1. Technology and innovation advantages 2. Can be mass-produced	1. Complex production process 2. High material cost and insufficient profitability
O (opportunities)	T (threats)
1. The automobile industry and the aerospace industry have a large demand for alloy materials with high strength and hardness 2. There are a wide range of consumer groups, and the product has a competitive advantage	1. The market is more competitive 2. The possibility of other alternative products is very high

Because the wear resistance and toughness of cemented carbide tool materials are not easy to take into account, users can only choose suitable tool materials from many cemented carbide grades according to the specific processing objects and processing conditions. This gives the choice and Management brings many inconveniences. In order to further improve the comprehensive cutting performance of cemented carbide tool materials, current research hotspots mainly include the following aspects:

- refine the grain

By refining the grain size of the hard phase, increasing the surface area between the hard phase crystals, and enhancing the bonding force between the grains, the strength and wear resistance of the cemented carbide tool materials can be improved. However, because the above-mentioned grain refinement process is still not mature enough, the

nano grains are easy to grow into coarse grains during the cemented carbide sintering process, and the general growth of the grains will cause the material strength to decrease, and a single coarse WC grain often It is an important factor causing material fracture. On the other hand, the price of fine-grained cemented carbide is relatively expensive, which also restricts its popularization and application.

- coated cemented carbide

On the tougher cemented carbide substrate, a thin layer of wear-resistant metal compound can be coated by CVD (Chemical Vapor Deposition), PVD (Physical Vapor Deposition), HVOF (High Velocity Oxy-Fuel Thermal Spraying) and other methods. Combine the strength and toughness of the substrate with the wear resistance of the coating to improve the overall performance of cemented carbide tools. Coated carbide tools have good wear resistance and heat resistance, and are especially suitable for high-speed cutting; due to their high durability and good versatility, they can effectively reduce the number of tool changes when used in small batches and multi-variety flexible automated processing , Improve processing efficiency; coated cemented carbide tools have strong anti-crescent wear resistance, stable cutting edge and groove shape, reliable chip breaking effect and other cutting performance, which is beneficial to the automatic control of the processing process; coated cemented carbide tools After the substrate is passivated and refined, the dimensional accuracy is high, which can meet the requirements of automatic machining for tool change positioning accuracy. The above characteristics determine that the coated carbide cutting tools are particularly suitable for automatic processing equipment such as FMS and CIMS (Computer Integrated Manufacturing System).

In summary, it is very promising and meaningful to invest in start-up companies for the idea of high-entropy alloy coated knives. The project's lead characteristic analysis is shown in table 7.6.

Table 7.6 - Characteristics of potential clients of the startup project

№	The need that shapes the market	Target audience (target market segments)	Differences in the behavior of different potential target customer groups	Consumer requirements for the product
	High entropy alloy blade	Coating tools can be used for drilling, tapping and cutting	The market demand is large, and the supply may be in short supply Affected by processing technology and global economy, the price is high	The matrix of the coated cemented carbide tool has high dimensional accuracy after passivation and refinement treatment, which can meet the requirements of automatic machining for tool change positioning accuracy.

7.4 Development of market strategy of the project

The development of a market strategy as a first step involves determining the strategy of market coverage: a description of target groups of potential consumers (Tabl. 7.7).

Table 7.7 - Selection of target groups of potential consumers

No	Description of the profile of the target group of potential customers	Readiness of consumers to accept the product	Estimated demand within the target group(segment)	Intensity of competition in the segment	Easy to enter the segment
	Coated tools can be used in drilling, tapping and cutting	Have confidence in the product and can accept it	High demand	Market competition is not fierce	Easy
Which target groups are selected:Automotive, aerospace, electronics, military and other industries that have large applications for coated tools					

Based on the analysis of the target group of potential consumers, the next step is to determine the basic marketing strategy of the project:

- improve the high-speed cutting performance of the blade to meet customers' high-efficiency processing needs

The hard blade industry is in the stage of adjustment and upgrading of the industrial structure. CNC machine tools are the upgrading trend of the machine tool industry. The rate of CNC machine tools in my country has maintained a steady growth in recent years. Downstream customers already have the equipment conditions for high-speed and efficient processing. The pursuit of processing efficiency is becoming more and more urgent. The improvement of processing efficiency puts forward higher requirements on the high temperature performance and wear resistance of CNC blades. The company improves and enhances the new performance of existing products while

satisfying the pursuit of processing efficiency by different customers through the application of grades. The company introduced substrates and coatings for high-efficiency turning processing. The products can achieve higher line speeds, depths of cut and feed, and achieve higher processing efficiency under the condition of unchanged service life.

- improve the stability and dimensional accuracy of CNC blades to meet the needs of customers for automated production

With the improvement of the degree of automation in the domestic machining industry, higher requirements are put forward for the stability and dimensional accuracy of CNC blades. In the face of this new development trend, the company actively adjusts and improves the existing production process, continuously improves the stability of product performance, and has also made breakthrough progress in the dimensional accuracy control of the special complex structure of cemented carbide blades. The company will continue to improve its processes to help customers automate production.

- consolidate and enhance the dominant position in the mold industry

As the basic process equipment used to make molded articles in industrial production, molds have a wide range of applications, and their manufacturing level has become one of the important indicators to measure the level of a country's manufacturing industry. The demand for molds is closely related to the remodeling and renewal needs of downstream electronic equipment, home appliances or automobiles, and the demand for molds in the market is huge. In the process of mold processing, frequent tool changes will not only cause low processing efficiency, but also cause tooling marks on the processed surface, which will affect the surface quality of the workpiece. Therefore, the

tools used in the mold processing industry need to maintain a stable service life while ensuring a high metal removal rate. This puts higher requirements on the groove design and dimensional accuracy control of the mold milling tools. In the future, the company will develop more excellent products based on the long-term accumulated experience in the development and application of mold milling cutters, and continue to consolidate and enhance its dominant position in the field of mold milling cutters.

- continue to expand the automotive industry market

The automotive industry is one of the main areas of cutting tool applications and has a broad market space. When selecting tools in the automotive industry, they have high requirements for the versatility of the tools. They need to meet the processing of different materials such as cast iron and steel during the processing. At the same time, affected by factors such as processing conditions, the blades are required to have good wear resistance at the same time. And impact resistance. In view of the above characteristics, the company will develop a more versatile groove structure, continuously improve the quality and service life of the blades, and expand the market space of the products in the automotive field.

- actively deploy the heavy-duty gravity machining tool market

With the large-scale construction of railway networks, especially high-speed railway networks, the demand for matching heavy-duty gravity machining tools has also expanded to varying degrees. At present, the company has solved the problem of the production process of heavy-duty gravity machining blades, and reserves part of the technology in the field of matrix materials and trough structure. The company will

develop more products with different functions and applications based on this, and achieve a breakthrough in the heavy-duty gravity tool market.

- layout the development of aerospace tool materials

The domestic aerospace industry tool market has long been dominated by foreign high-end brands. It is urgent to improve the independent support capability of aerospace tools. The rapid development of the aerospace industry is bound to drive the growth of demand for high-end cutting tools. Aerospace materials are mostly high-performance difficult-to-machine materials. For this market, the company will focus on the research and development of cemented carbide substrates and PVD coating materials. Continuous improvement in groove and boundary wear, material performance, etc.

7.5 Conclusion

Hard blades have a wide range of applications, including automobiles, rail transit, aerospace, precision molds, energy equipment, engineering machinery, general machinery, petrochemicals, electronic information technology and other fields. They are an important part of national industry and manufacturing. Industry development is closely related. Due to the parts that work under high temperature, high pressure, high speed, and corrosive fluid media, more and more difficult-to-machine materials are used, and the automation level of cutting processing and the requirements for machining accuracy are getting higher and higher. In order to adapt to this situation, the development direction of cemented carbide tools will be the development and application of new cemented carbide tool materials; further

develop the vapor deposition coating technology of cemented carbide tools, and deposit higher on the substrate with high toughness and high strength. The hardness coating can better solve the contradiction between the hardness and strength of the cemented carbide tool material; further develop the structure of the indexable cemented carbide tool; improve the manufacturing accuracy of the cemented carbide tool, reduce the difference in product quality, and increase the usage rate of cemented carbide tools.

CONCLUSIONS

In this paper, a series of AlNiCoFeCrTiMo high-entropy alloys were prepared by mechanical alloying and sintering methods. The microstructure, phase composition and properties of AlNiCoFeCrTiMo high-entropy alloys prepared by mechanical alloying and different sintering processes were studied respectively. In the end, the following main conclusions can be drawn:

1. An important literature review shows that high-entropy alloys (HEAs) have aroused great interest in materials science and engineering because of their unique structures and properties.
2. In order to manufacture AlNiCoFeCrTiMo HEA powder, mechanical alloying technology is applied. Tests have proved that the AlNiCoFeCrTiMo high-entropy alloy prepared by MA-SPS has higher strength and hardness.
3. Use various characterization methods (scanning electron microscope SEM, Ultima IV X-ray diffractometer XRD, Vickers microhardness machine PMT-3 and microtester Micron Gamma machine capable for load-displacement measurements) to determine the morphology, microstructure, phase composition as well as microhardness and other mechanical properties.
4. Use the NETZSCH differential scanning calorimeter to measure the differential scanning calorimetry signal (DSC) curve of the alloy from room temperature to 1400 °C, and obtain the phase transition information of the high-entropy alloy powder obtained by mechanical alloying during the heating process.

5. Comparing the microstructure and mechanical properties of pressure sintering and SPS sintered HEA, it can be concluded that, the high-entropy alloy prepared by pressure sintering has better microstructure and high mechanical properties.

6. The labor safety protection part of the test process is summarized, and the possible safety hazards and the handling methods of unexpected emergencies in the test process are analyzed.

7. Calculated the economic costs of energy, manpower, materials and some other costs during the test, then compared with the predicted economic efficiency to prove the feasibility of the master's thesis test.

REFERENCES

- [1] Rapid Solidification Processing[J]. / L. A. Jacobson, J. M. Kittrick. // Materials Science and Engineering R, 1994,11(8) : 355-408.
- [2] High-tech Coating for Turbine Blades[J]. / A. Stenve. // Mechanical Engineering, 1995(10) : 66-69.
- [3] Rheocasting[J]. / M. C. Flemings, Riekrig Youngkp. // Materials Science and Engineering, 1976,25 : 103-117.
- [4] Semi-solid metalworking and its application. / Xie Aquatic, Huang Shenghong. // Beijing: Metallurgical Industry Press, 1999 : 10-45.
- [5] Continuous Series of Metastable solid Solution in Silver Copper Alloys[J]. / P. Duwez, R. H. Willens, W. Klement. // Journal of Applied Physics, 1960,31 : 1136-1137.
- [6] Microstructural and Mechanical Characteristics of In Situ Metal Matrix Composites[J]. / S. C. Tjong, Z. Y. Ma. // Materials Science and Engineering R, 2000,29 : 49~113
- [7] Confusion by design [J]. / Greer A L. // Nature, 1993, 366(6453): 303-304.
- [8] Microstructural development in equiatomic multicomponent alloys [J]. / Cantor B, Chang I T H, Knight P, et al. // Materials Science and Engineering A, 2004, 375-377 : 213-218.
- [9] A critical review of high entropy alloys and related concepts [J]. / Miracle D B, Senkov O N. // Acta Materialia, 2017, 122 : 448-511.
- [10] Carbothermal shock synthesis of high-entropy-alloy nanoparticles [J]. / Yao Y, Huang Z, Xie P, et al. // Science, 2018, 359(6383) : 1489-1494.

- [11] Irradiation resistance of multicomponent alloys [J]. / Egami T, Guo W, Rack P D, et al. // *Metallurgical and Materials Transactions A*, 2013, 45(1) : 180-183.
- [12] Elucidating the Microstructural and Tribological Characteristics of NiCrAlCoCu and NiCrAlCoMo Multicomponent Alloy Clad Layers Synthesized In Situ[J]. / Y. C. Lin, Y. H. Cho. // *Surface & Coatings Technology*, 2009, 203 : 1694-1701.
- [13] Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes [J]. / Yeh J W, Chen S K, Lin S J, et al. // *Advanced Engineering Materials*, 2004, 6(5) : 299-303.
- [14] Progress in the phase-forming of multi-main-component high-entropy alloys. / Li Wenhui, Ai Tao. // *Powder metallurgy industry*, 2016, 26 (1) : 64-67
- [15] High-Entropy Alloys: Fundamentals and Application [M]. / Zhang Y, Cao M, Yeh J, et al. // Berlin: Springer, 2016
- [16] A promising new class of high-temperature alloys: eutectic high-entropy alloys [J]. / Lu Y P, Dong Y, Guo S, et al. // *Scientific Reports*, 2014, 4 : 1-5.
- [17] Explore the possibility of forming fcc high entropy alloys in equal-atomic systems CoFeMnNiM and CoFeMnNiSmM [J]. / C.-h. Zhang, M.-h. Lin, B. Wu, et al. // *Journal of Shanghai Jiaotong University (Science)*, 2011, 16(2) :173-179.
- [18] Study on the preparation and structure and performance of multi-main high entropy alloys. / Liu Wenjie. // Shenyang: Northeastern University, 2010, 1-2.
- [19] AlCoCrFeNiTi (0.5) High entropy alloy tissue control and corrosive energy. / Yu Yuan, Xie Faqin, Zhang Tiebang, etc. // *Rare Metal Materials and Engineering*, 2012, 41 (5) : 862-866.

- [20] Microstructures and properties of high-entropy alloys [J]. / Zhang Y, Zuo T, Calcarente, Tang Z, et al. // Progress in Materials Science, 2014, 61 : 1-93.
- [21] Formation of ordered/disordered nanoparticles in FCC high entropy alloys [J]. / Shun T Calcarente, Hung C H, Lee C F. // Journal of Alloys and Compounds, 2010, 493(1) : 105-109.
- [22] Alloyed pleasures: Multimetallc cocktails [J]. / Ranganathan S. // Research News, 2003, 85 : 1404-1406.
- [23] Effects of Al addition on the microstructure and mechanical property of $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloys [J]. / Wang W. R, Wang W L, Wang S C, et al. // Intermetallics, 2012, 26 (7) : 44-51. 49
- [24] On Lattice Distortion in High Entropy Alloys. / He Q and Yang Y (2018) // Front. Mater. 5:42.
- [25] Effects of Al addition on structure evolution and tensile properties of the FeCoNiCrMn high-entropy alloy system[J]. / He J Y, Liu W H, Wang H, et al. // Acta Materialia, 2014, 62 : 105-113.
- [26] Effect of annealing treatment on phase composition and microstructure of CoCrFeNiTiAl_x high-entropy alloys [J]. / Zhang K B, Fu Z Y. // Intermetallics, 2012, 22 : 24-32
- [27] A hexagonal close-packed high-entropy alloy: The effect of entropy [J]. / Zhao Y J, Qiao J W, Ma S G, et al. // Materials & design, 2016, 96(Apr.) :10-15.
- [28] Research Progress of Laser Cladding High-Entropy Alloy Coating[J]. / Liufei Huang, Yaoning Sun, Guojian Wang. // Laser & Optoelectronics Progress, 2019, 56(24) : 240003(in chinese)

- [29] On the Evidence of Thermodynamic Self-Organization during Fatigue: A Review[J]. / Mehdi Naderi. *Entropy*. 2020(3)
- [30] Phase transformation and mechanical behavior of TiFeCoNi alloy during annealing [J]. / Tsau C H. // *Materials Science & Engineering A*, 2009, 501(1-2) : 81-86.
- [31] Synthesis and thermal stability of a nanocrystalline MoNbTaTiV refractory high-entropy alloy via mechanical alloying[J]. / Wang G F, Liu Q, Yang J L, et al. // *International Journal of Refractory Metals & Hard Materials*, 2019, 84 : 104988.
- [32] Effect of Nb addition on the microstructure and properties of AlCoCrFeNi highentropy alloy [J]. / Ma S G, Zhang Y. // *Materials Science & Engineering A*, 2012, 532(1) : 480-486.
- [33] Tensile properties of high- and medium-entropy alloys [J]. / Gali A, George E P. // *Intermetallics*, 2013, 39(4) :74-78.
- [34] A novel, single phase, non-equiatomic FeMnNiCoCr highentropy alloy with exceptional phase stability and tensile ductility [J]. / Yao M J, Pradeep K G, Tasan C Gail, et al. // *Scripta Materialia*, 2014, 72-73(1) : 5-8.
- [35] Resent Development in High-Entropy Alloys and Other High-Entropy Materials[J]. / Xiao-peng Wang and Fan-tao Kong. // *Journal of Aeronautical Materials*.
- [36] Effect of Ti content on structure and properties of Al₂CrFeNiCoCuTi_x high-entropy alloy coatings [J]. / Qiu X W, Zhang Y P, Liu C G. // *Journal of Alloy Componend*, 2014, 585 : 282-286.
- [37] Microstructural evolution, electrochemical and corrosion properties of

$\text{Al}_x\text{CoCrFeNiTi}_y$ high entropy alloys [J]. / Qiu Y, Thomas S, Fabijanic D, et al. // Material & Design, 2019, 170(15) : 107698.

[38] In vitro and in vivo studies on biodegradable CaMgZnSrYb high-entropy bulk metallic glass[J]. / Li H.F., Xie X.H., Zhao K., et al. // Acta Biomaterialia, 2013, 9 (10) : 8561-8573

[39] Characterization of multi-principal-element $(\text{TiZrNbHfTa})\text{N}$ and $(\text{TiZrNbHfTa})\text{C}$ coatings for biomedical applications[J]. / Braic V., Balaceanu M., Braic M., et al. // Journal of the Mechanical Behavior of Biomedical Materials, 2012, 10 : 197-205

[40] Irradiation resistance of multicomponent alloys[J]. / Egami T., Guo W., Rack P.D., et al. // Metallurgical and Materials Transactions A, 2014, 45(1) : 180-183

[41] Hydrogen storage properties of multi-principal-component $\text{CoFeMnTi}_x\text{V}_y\text{Zr}_z$ alloys[J]. / Kao Y.F., Chen S.K., Sheu J.H., et al. // International Journal of Hydrogen Energy, 2010, 35(17) : 9046-9059

[42] High entropy alloy as a highly active and stable electrocatalyst for hydrogen evolution reaction [J]. / Zhang G, Ming K, Kang J, et al. // Electrochimica Acta, 2018, 279 : 19-23. 50.

[43] First hexagonal close packed high-entropy alloy with outstanding stability under extreme conditions and electrocatalytic activity for methanol oxidation[J]. / Yuseenko K V, Riva S, Carvalho P A, et al. // Scripta Materialia, 2017, 138 : 22-27.

[44] Irradiation resistance in $\text{Al}_x\text{CoCrFeNi}$ high entropy alloys [J]. / Xia S Q, Yang X, Yang T F, et al. // JOM, 2015, 67(10) : 2340-2344.

[45] New progress in research on high-well alloys and other high-entropy

- materials[J]. / Wang Xiaopeng, Kong Fantao. // Journal of Aeronautical Materials, 2019, 39(6) : 1-19.
- [46] The current research status of powder high temperature alloy in China. / Zhang Yiwen, Yang Shizhong, Li Shushing. // Material Guide, 2002, 16 (5) : 1-4.
- [47] Robust zero resistance in a superconducting high-entropy alloy at pressures up to 190 GPa [J]. / Guo J, Wang H, Rohr F von, et al. // Proceeding of the National Academy of Sciences of the United States of America, 2017, 114(50) : 13144-13147.
- [48] Progress in Preparation and Research of High Entropy Alloys. / CHEN Yong-xing, ZHU Sheng, WANG Xiao-ming, DU Wen-bo, ZHANG Yao. // Journal of Materials Engineering, 2017, 45(11) : 129-138.
- [49] Advances in the study of multi-main high entropy alloys. / Guo Weifan. // Metal functional materials, 2009, 16 (1) : 49.
- [50] Principles, characteristics and research progress of high-speed suppression technology of powder metallurgy. / Shen Yuanxun, Xiao Zhiyu, Wen Liping, etc. // Powder Metallurgy Industry, 2006, 16 (3) : 19.
- [51] Research status of laser additive manufacturing steel powder materials. / Dong Shiyun, Yan Shixing, Feng Xiangyi, Li Yongjian, Chen Suiyuan. // Progress in Laser and Optoelectronics. 2018 Sep 10;55(1) : 011407.
- [52] Microstructure and properties of sintered AlNiCrFeCuMox alloys[J]. / GUAN Hongyan , ZHANG Yunpeng , FAN Yuhu , et al. // Rare Metal Materials and Engineering, 2012, 41(S2) : 532.
- [53] The organization and properties of the AlCrMnMoNiZr (B0.1) alloy prepared

by powder metallurgy. / Zhao Ruifeng, Li Hongju, Ren Bo, etc. // *Special Casting and Non-ferrous Alloys*, 2013, 33 (3) : 288.

[54] Powder metallurgy of high-entropy alloys and related composites: A short review. / Bo-ren Ke, Yu-chen Sun, Yong Zhang, Wen-rui Wang, Wei-min Wang, Pei-yan Ma, Wei Ji, and Zheng-yi Fu. // *Int. J. Miner. Metall. Mater.*, 28(2021), No. 6, pp. 931-943.

[55] *Intermetallics*, 56, W. Ji, W.M. Wang, H. Wang, J.Y. Zhang, Y.C. Wang, F. Zhang, and Z.Y. Fu / Alloying behavior and novel properties of CoCrFeNiMn high-entropy alloy fabricated by mechanical alloying and spark plasma sintering // 24-27, Copyright 2015, with permission from Elsevier.

[56] Nanocrystalline CoCrFeNiCuAl high-entropy solid solution synthesized by mechanical alloying[J]. / Zhang K B, Fu Z Y, Zhang J Y, et al. // *Journal of Alloys and Compounds*, 2009, 485 : L31-L34.

[57] Microstructure and strengthening mechanisms in an FCC structured single-phase nanocrystalline $\text{Co}_{25}\text{Ni}_{25}\text{Fe}_{25}\text{Al}_{7.5}\text{Cu}_{17.5}$ high-entropy alloy [J]. / Fu Z, Chen W, Wen H, et al. // *Acta Materialia*, 2016, 107 : 59-71.

[58] Deformation twinning structure and interface in an FCC-based $\text{Al}_{0.3}\text{FeNiCo}_{1.2}\text{CrCu}$ high-entropy alloy matrix composites[J]. / Yang S, Pi J, Yang W, et al. // *Materials Letters*, 2018, 214 : 50-52.

[59] The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. / Munir Z A, Anselmi-Tamburini U, Ohyanagi M. // *J Mater Sci*, 2006, 41(3) : 763

[60] Improved Manufacture of Electric Incandescence Lamp Filaments from

- Tungsten or Molybdenum or an Alloy. / Lux J. // US Patent, 27002. 1906
- [61] Electric-discharge Sintering / Inoue K. // US Patent, 3241956. 1966-3-22
- [62] Joining of Silicon Carbide Ceramic by Hybrid Spark Plasma Sintering. / Sorokin, Oleg & Vaganova, M. & Solntsev, S. & Osin, I. // Russian Journal of Applied Chemistry. 88. 839-845. 10.1134/S1070427215050183.
- [63] Spark plasma sintering technology. / Bai L, Ge C C, Shen W P. // Powder Metall Technol, 2007, 25(3) : 217
- [64] Advances in the preparation of thermoelectric materials by mechanical alloying combined with discharge plasma sintering technology. / Shi Jianlei, Yan Jun, Zhang Boping, Li Jingfeng. // Powder Metallurgy Technology, 2021, 39 (01) : 4-14.
- [65] Electrical and thermal transport properties of spark plasma sintered n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ alloys: the combined effect of point defect and Se content. / Pan Y, Wei T R, Wu C F, et al. // J Mater Chem C, 2015, 3(40) : 10583
- [66] Alloying behavior and novel properties of CoCrFeNiMn high-entropy alloy fabricated by mechanical alloying and spark plasma sintering[J]. / Ji W, Wang W, Wang H, et al. // Intermetallics, 2015, 56 : 24-27.
- [67] Formation and Stability of Equiatomic and Nonequiatomic Nanocrystalline CuNiCoZnAlTi High-Entropy Alloys by Mechanical Alloying[J]. / Varalakshmi S, Kamaraj M, Murty B S. // Metallurgical & Materials Transactions A, 2010, 41(10) : 2703-2709.
- [68] Hot consolidation and mechanical properties of nanocrystalline equiatomic AlFeTiCrZnCu high entropy alloy after mechanical alloying[J]. / Varalakshmi S,

- Rao G A, Kamaraj M, et al. // Journal of Materials Science, 2010, 45(19) : 5158-5163.
- [69] Study on mechanical alloying and annealing behavior of AlFeCrCoNi high entropy alloys. / Wei Ting, Chen Jian, Wang Zhaoqiang, et al. // Journal of Xi'an University of Technology, 2015, (2) : 162-166.
- [70] New technologies for surface processing of materials and their products. / Li Guoying. // Changsha: Zhongnan University Press, 2003.
- [71] Study on the organization and performance of the high entropy alloy coating of the CrNiAlCoMoB_x system of laser cladding application laser. / Yu Pengjin, Dong Gang, Yao Jianhua. // 2015, 35 (1) : 1.
- [72] Study on the organization and performance of high entropy alloys of laser cladding preparation Ti_xFeCoCrWSi. / An Xulong. // Guiyang: Guizhou University, 2015.
- [73] Laser cladding FeCoNiMnMoxB0.5 high entropy alloy coating tissue and corrosion resistance. / Li Dongliang, Zhou Fang, Yu Shihao. // Strong Laser and Particle Beam, 2016, 28 (2) : 1.
- [74] The tissue and properties of the laser cladding AlCoCrCu0.5FeMoNiTi high entropy alloy coating. / Wen Lizhe, Huang Yuansheng. // Powder Metallurgy Technology, 2016, 34 (4) : 268.
- [75] High temperature wear performance of laser-cladded FeNiCoAlCu high entropy alloy coating [J]. / Jin G, Cai Z B, Guan Y J, et al. // Applied Surface Science, 2018, 445 : 113-122.
- [76] Review on preparation and application of high-entropy alloy coatings[J]. /

- ZHAO Qin, MA Guo-zheng, WANG Hai-dou, et al. // Materials reports, 2017, 31(7) : 65-71.
- [77] Solid-solution CrCoCuFeNi high-entropy alloy thin films synthesized by sputter deposition[J]. / AN Z, JIA H, WU Y, et al. // Materials research letters, 2015, 64 : 1-7.
- [78] Multi-principal-element alloys with improved oxidation and wear resistance for thermal spray coating[J]. / HUANG P K, YEH J W, SHUN T Croconic, et al. // Advanced engineering materials, 2004, 6(1-2) : 74-78.
- [79] Plasmasprayed high entropy alloys: Microstructure and properties of AlCoCrFeNi and MnCoCrFeNi[J]. / ANG A S M, BERNDT C C, SESSO M L, et al. // Metallurgical and materials transactions A, 2015, 46(2) : 791-800.
- [80] Research progress of high-entropy alloy coatings[J]. / Huang Can, Du Cuiwei, Dai Chunduo, Ma Zheng, Liu Zhiyong, Li Xiaogang. // Surface Technology, 2019, 48(11) : 15-22+35.
- [81] Overview of research on defect formation mechanism and microstructure control of thermal spray coatings[J]. / Zhou Chaoji, Zhu Sheng, Wang Xiaoming, Han Guofeng, Zhou Keping, Xu Anyang. // Materials Review, 2018, 32(19) : 3444-3455 +3464.
- [82] Advanced cold spray technology: deposition characteristics and potential applications [J]. / Wu X K, Zhang J S, Zhou X L, et al. // Science China Technological Sciences, 2012, 55(2) : 357-368.
- [83] Significant influence of carrier gas temperature during the cold spray process [J]. / Yin S, Suo X, Liao H, et al. // Surface Engineering, 2014, 30(6) : 443-450.

- [84] Strong effect of carrier gas species on particle velocity during cold spray processes [J]. / Suo X, Yin S, Planche M P, et al. // Surface and Coatings Technology, 2015, 268 : 90-93.
- [85] Guangzhou Sanxin Metal Technology Co., Ltd
<http://www.sx020.com/product/273.html>
- [86] Quantitative prediction of critical velocity and deposition efficiency in cold-spray: A finite-element study [J]. / Meng F C, Yue S, Song J. // Scripta Materialia, 2015, 107 : 83-87.
- [87] Beneficial effects of laser irradiation on the deposition process of diamond/Ni60 composite coating with cold spray [J]. / Yao J H, Yang L J, Li B, et al. // Applied Surface Science, 2015, 330 : 300-308.
- [88] A differential scanning calorimetric investigation of precipitation kinetics in the Al-1.53 wt% Cu-0.79 wt% Mg alloy / A.K. Jena, A.K. Gupta, M.C. Chaturvedi // Acta Metall., 1989, 37 : 885-889
- [89] An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. / Oliver, W.C.; Pharr, G.M. // J. Mater. Res. 1992, 7, 1564-1583.
- [90] Automated indentation to establish ultimate hardness, elastic strain, and associated stress of materials. / S. A. Firstov, V. F. Gorban', and É. P. Pechkovskii. // Materialovedenie, 2008, No. 8 : 15–21.
- [91] Structure and Mechanical Properties of High-Entropy AlCuNiFeTi and AlCuNiFeCr Alloys Produced by Mechanical Activation Followed by Pressure

Sintering. / Yurkova A.I., Chernyavskii V.V., Gorban V.F. // Powder Metallurgy and Metal Ceramics. 2016, Volume 55, Issue 3, pp 152–163.

[92] Competition between elements during mechanical alloying in an octonary multi-principal-element alloy system[J]. / Chen Y.L., Hu Y.H., Hsieh C.A., et al. // Journal of Alloys and Compounds, 2009, 481 (1-2) : 768-775

[93] Microstructure and nanoscale composition analysis of the mechanical alloying of $\text{Fe}_x\text{Cu}_{100-x}$ ($x = 16, 60$). / Huang, J.Y. // Acta Mater. 45, 1997, 113–124. (Huang J.Y., Y.D. Yu, Y.K. Wu, D.X. Li, H.Q. Ye)

[94] Structure formation and mechanical properties of high-entropy AlCuNiFeCr alloy prepared by mechanical alloying and spark plasma sintering. / Yurkova A.I., Chernyavsky V.V., Bolbut V., Krüger M., Bogomol I.

[95] Journal of Alloys and Compounds. – 2019. – V. 786. – P. 139-148. (Scopus, WoS) <https://doi.org/10.1016/j.jallcom.2019.01.341>

[96] Character-ization of nanocrystalline CoCrFeNiTiAl high-entropy solid solution processed by mechanical alloying[J]. / K.B. Zhang, Z.Y. Fu, J.Y. Zhang, W.M. Wang, S.W. Lee, K. Niihara. // Alloys Compd. 459 (2010) 33-38.

[97] Mechanical alloying synthesis and spark plasma sintering consolidation of CoCrFeNiAl high-entropy alloy[J]. / W. Ji, Z. Fu, W. Wang, H. Wang, J. Zhang, Y. Wang, F. Zhang. // Alloys Compd. 589 (2014) 61-66.

[98] Research Progress on Mechanical Properties of High Entropy Alloys. / Li, A. & Shi, J. & Xie, M.. (2018). // Cailiao Daobao/Materials Review. 32. 461-466 and 472. 10.11896/j.issn.1005-023X.2018.03.017.

- [99] LTO 3.3.6-042-99. / State sanitary norms of microclimate of industrial premises.
- [100] On approval of the Rules of labor protection in heat treatment of metals. / <https://zakon.rada.gov.ua/laws/show/z0066-08#Text>
- [101] DBN B.2.2-28: 2010 Administrative and domestic buildings. <https://dbn.co.ua/load/normativy/dbn/1-1-0-806>
- [102] DBN B.2.5-67: 2013. Heating, ventilation and air conditioning (32609) https://dnaop.com/html/32609/doc-%D0%94%D0%91%D0%9D_%D0%92.2.5-67_2013
- [103] Levchenko OG, Polukarov OI Labor protection in welding production: Textbook. K.: Osnova, 2014. 352 p.
- [104] DNAOP 0.00-1.21-98. Rules for safe operation of electrical installations of consumers.
- [105] NPAOP 28.0-1.37-14. Rules of labor protection at drawing metal coverings.
- [106] PUE-2017. Rules of arrangement of electrical installations. - Kyiv: Ministry of Energy and Coal of Ukraine, 2017. - 617 p.
- [107] NAPB B.03.002-2007. Determining the category of premises, buildings and outdoor installations according to explosion and fire hazard.

ЗАУВАЖЕННЯ
до магістерської дисертації студентки
Шао Їжу

№	Зауваження	Відмітка
	ТИТУЛКА	
1	Відсутні консультанти з розділу охорони праці в надзвичайних ситуаціях; з організаційно-економічного розділу та нормоконтролю	ТИТУЛКА
	ЗАВДАННЯ	
2	Відсутній строк подання роботи	ЗАВДАННЯ
3	Відсутній номер наказу	ЗАВДАННЯ
	ЗМІСТ	
4	ABSTRACT не вносять до ЗМІСТу	ЗМІСТ
5	Відсутній розділ «ЕНЕРГЕТИЧНИЙ РОЗДІЛ»	ЗМІСТ
6	“CONCLUSIONS”, «REFERENCES» не нумеруються	ЗМІСТ, С.106, 108
	ТЕКСТ РОБОТИ	
7	Розділ починають з нової сторінки	
8	Назву рисунку треба друкувати по центру рядка без абзацного відступу	С.18,23,24,25,28, 31,63
9	Назви підрозділів, таблиць, пояснень до формул друкують з абзацного відступу	С.43,44
10	Назви розділів та підрозділів тощо друкують один за одним без порожнього рядка між ними	С.11,12,13,15,16
11	Назви розділів, підрозділів, пунктів, підпунктів тощо відокремлюють від тексту до і після одним порожнім рядком	С.63
12	Тест не можна відривати від назв розділів, підрозділів, пунктів, підпунктів тощо	С.20,30,49,50,58,60, 66,83,87,98,101
13	Пояснення до позначень, наведених на рисунку друкують по центру рядка без абзацного відступу перед назвою рисунку	С.18,31
14	По всьому 4, 5, 6 розділах не правильна нумерація підрозділів	С.68-78, 79-94, 95-105
15	Крапку у кінці назв розділів, підрозділів тощо, рисунків, таблиць не ставлять	С.18,34
16	Крапку після номера розділів, підрозділів тощо, рисунків, таблиць не ставлять	ЗМІСТ, С.11,43
17	Переліки виконати у відповідності до ДСТУ 3008-2015	С.38,40,75,76,88, 90-93,
18	Посилання на рисунки та таблиці, які записують у круглих дужках мають скорочену форму (рис. 3.2, табл. 5.1)	С.24
19	Посилання на рисунки та таблиці у контексті речення записують повністю (на рисунку 3.2, у таблиці 5.1)	С.21,23,25,28,55,58, 60,63,65
20	Опис бібліографічних джерел виконують відповідно до ДСТУ ГОСТ 7.1:2006	С.108-121
	ПРЕЗЕНТАЦІЯ	
21	Відсутня нумерація слайдів - необхідно додати	ПРЕЗЕНТАЦІЯ
22	Занадто багато слайдів МАКСИМУМ 15 СЛАЙДІВ!!!	ПРЕЗЕНТАЦІЯ
23	Деталізувати таблиці і підписи до них	ПРЕЗЕНТАЦІЯ

Відповідальний за нормоконтроль
кафедри ВТМ та ПМ

Троснікова І.Ю.