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High entropy alloys

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In this paper we will present an overview of high entropy alloys and also will expose the research to date on these alloys. It should be mentioned that High Entropy Alloys are characterized as alloys consisting of roughly equal concentrations of at least five metallic elements and are claimed to favor close-packed, disordered structures due to high configurational entropy. Such crystal structures, e.g. face-centered cubic (FCC), are advantageous in that they should offer multiple active slip systems usually observed in ductile metals and alloys. This opens the door to a large number of rich chemistries which would otherwise contain unacceptable volume fractions of intermetallic compounds to be useful in structural applications.This paper is divided into several chapters which will present some general properties of alloys, application domains, and also a number of conclusions. In short we try to give some answers to frequently asked questions about this new area.

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Keywords: High entropy alloys, Properties of alloys, Application domains

1. Introduction

The initiator of the new concept ‘"high" entropy alloys is Yeh that in 1995 suggested the formation of an alloy consisting of at least five metallic elements, elements that have large mixing entropy solutions with many elements forming solide alloys. This alloy has appeared due to the fact that traditional alloys have a high fragility and difficulty processing.

We could define high entropy alloys as alloys which have approximately equal concentrations, formed by a group of 5 to 11 elements majority in composition, mole fraction of each major metallic element in the alloy is between 5% and 30%. As main elements we can use metals like: aluminum (Al), scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe) , cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), rutheniu (Ru), rhodium (Rh) , palladium (Pd), silver (Ag), hafnium (Hf), tantalum (Ta), tungsten (W), platinum (Pt), gold (Au), lanthanum (La), cerium (Ce) and so on. In addition to these metals we can add so-called minority elements, because their molar fraction in the alloy is less than 3.5%. A high entropy alloy elements can be metallic or nonmetallic minority, these elements can be selected from the following elements: lithium, sodium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, strontium, yttrium, zirconium, niobium, molybdenum, rutheniu, rhodium, palladium, silver, cadmium, indium, platinum, gold,bismuth, lanthanum metal . Non-metallic elements may be for example carbon, boron, silicon, phosphorus, sulfur, hydrogen, oxygen, nitrogen and so on. (Huang, Yeh, Shun, Chen 2004; Ranganathan 2003).

In alloys with high entropy will be no element mole fraction greater than 30% so there will be no metal matrix in alloy composition. Studies of high entropy alloys have shown that they have a almost amorphous structure demonstrated by X-ray diffraction and differential scanning calorimetric analysis. HEA has a high atomic disorder with mechanical properties comparable to the glass therefore are brittle. (Yeh,Chen, Lin, Gan, Chin, Shun, 2004).

The research performed showed that this alloy exhibits high hardness and corrosion resistance and good thermal stability as well. (Chen ,Wong, 2008).

It was noted that this type of alloy will form a single phase solid solution with a cubic crystal structure instead of multiple intermetallic phases, especially at high temperatures. This trend is explained by high entropy of the second principle of thermodynamics. The second principle of thermodynamics specifies the conditions in which the heat energy convert in mechanical energy. (Cantor, Chang, Knight Vincent, 2004).

High entropy alloys show properties superior to the conventional alloys. For this reason, HEA can be used in many applications that require resistance, thermal stability and resistance, wear and oxidation temperature application up to 800 ° C tools, forms, dies, machine parts and oven parts , etc.

2. Thermodynamical Considerations

High entropy alloys (HEA) do not have in composition a metal which is dominant and it can be matrix for crystallization and solidification. The simultaneous presence of at least 5 elements close to molar concentration, leads to an alloy with a high atomic disorder and with a micro /

nanocrystalline and even amorphous structure and mechanical properties close the glass.

According to the second principle of thermodynamics in isolated systems are produced only those transformations which accentuate disorder and which lead to increasing entropy and decreasing enthalpy and free energy.

Starting from the consideration that the alloys are practically incompressible and at constant volume free energy F can be defined by Helmholtz's relationship:

$$F = E - TS \tag{1}$$

in which: E- free energy; S- enthalpy; T- absolute temperature , it can lead to an expression that takes into account the contribution of the temperature for internal energy and entropy increasing :

$$F = \left(E_0 + \int_0^T CpdT \right) - T\left(S_0 + \int_0^T Cp\frac{dT}{T} \right) \tag{2}$$

where: E_o = is the internal energy at zero, K;

S_0 = enthalpy configuration;

Cp = specific molar heat at constant pressure.

If the temperature is associated with the dependent terms and with the terms expressing the vibration energy of the crystalline network and the thermal entropy in function $f(c,T)$, where c is the atomic fraction concentration, then:

$$F = E_0 - TS_0 + f(c,T) \tag{3}$$

$f(c,T)$ depends on the chemical composition of the alloy because according to the rule Neumannn - Kapp the specific heat can be approximated with the weighted average specific heat values of the components.

For liquid and solid solutions composed of 5 elements in a molar ratio, the variation of the configurational entropy with the number of moles can be calculated using the Boltzmann equation:

$$S_0 = k \ln W \tag{4}$$

where: K= Boltzmann's constant;

W= number of possible states in the system.

Entropy of configuration varies with atomic concentration , so:

$$S_0 = -R[c \ln c + (1-c)\ln(1-c)] \tag{5}$$

where: $R = 8{,}314\, J/mk$ - universal gas constant.

Solving the equation (5) will lead to the following results:

$S_0 = 11{,}52\, J/k$ for binary systems;

$S_0 = 15{,}86\, J/k$ for ternary systems;

$S_0 = 18{,}70\, J/k$ for quaternary systems;

$S_0 = 20{,}79\, J/k$ for quinary systems;

$S_0 = 22{,}45\, J/k$ for systems with six elements.

It is found that the introduction of a new element leads to a great increase of the configurational entropy, and the value continues to grow as new elements are added to the system.

Since for HEAs with at least five elements the configurational entropy is double compared to that of binary systems, they are called "high entropy alloys''.

3. Experimental Details

The alloy obtained and investigated in this paper is AlFeCrMnNi. For the preparation of this alloy an 8000 Hz medium frequency induction furnace was used (Fig.1).

Fig.1. Induction heating furnace of medium frequency (8000 Hz).

Crucible induction furnaces are used for the elaboration of high-quality steels, cast iron, non-ferrous metals and alloys such as aluminum, copper, nickel, etc.

In terms of supply voltage frequency, crucible furnaces include:

• Industrial frequency (50 Hz)
• Medium frequency (100 ... 10,000 Hz)
• High frequency (50 ... 400 kHz)

The current capacity for industrial frequency furnaces has values between 0.8 to 50 t, the power reaches 20 to 25 MW, the specific consumption of electricity is 520 to 700 kWh /t (Dan Comşa et al., 1979).

The main components of crucible furnaces are:

- Crucible
- Inductor
- Magnetic shield
- Short network - comprised of flexible cables and power supply rails
- Reversal mechanism.

Items shown in figure (2) (Dan Comşa et al., 1979).

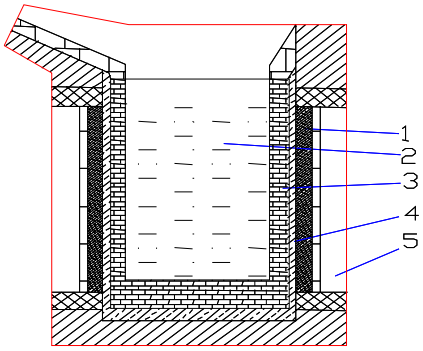


Fig. 2. Schematics of induction heating crucible furnace: 1 – inducer, 2 - molten metal, 3 - refractory crucible, 4 - asbestos cylinder, 5 - ferromagnetic screens.

The chemical composition of the alloy is : 36 % Fe, 22,19% Cr, 23,67% Mn, 13,76% Ni, 3.52% Al.

The melting temperature of the alloy was between 1530-1580° C. The alloy was cast and cooled in a metallic mold. The obtained samples were subjected to mechanical characterization tests.

4. Results

The sample to be analyzed was previously polished and etched with Villela's reagent.

4.1. Analysis by scanning electron microscope

After microstructural analysis it could be observed that the grains are polygonal and have non-uniform sizes. The following figures present the microstructure of the alloy at different SEM magnifications. The non-uniform polygonal grains (Fig. 3a) and grain boundaries (Fig.3b) are highlighted in Fig. 3.

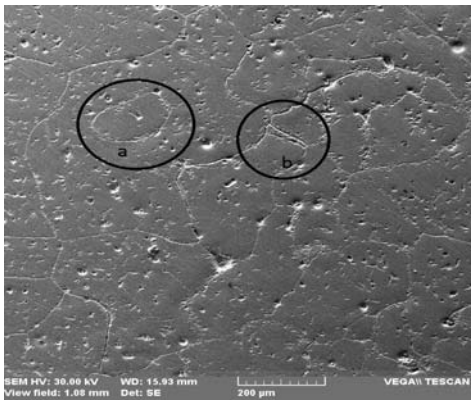


Fig. 3. SEM analysis of AlFeCrMnNi X250 power x250 alloy: a) non-uniform polygonal grains, b) grain limits.

In the following micrographs both non-uniform polygonal grains and grain limits can be seen at various magnifications.

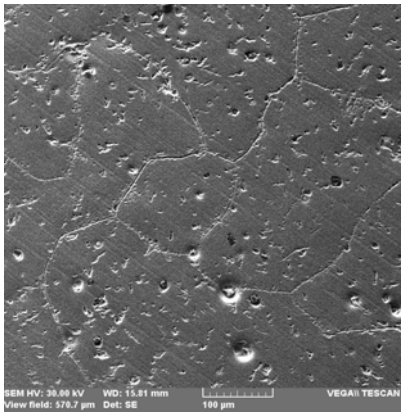


Fig. 4. Image SEM 500x

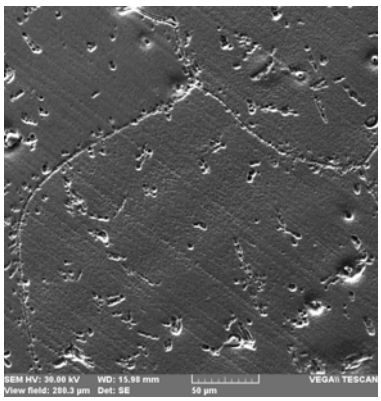


Fig. 5. ImageSEM 1kx

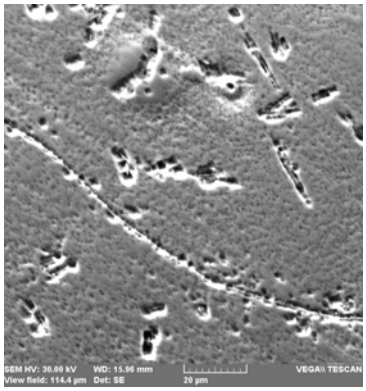


Fig. 6. Image SEM 2.5kx

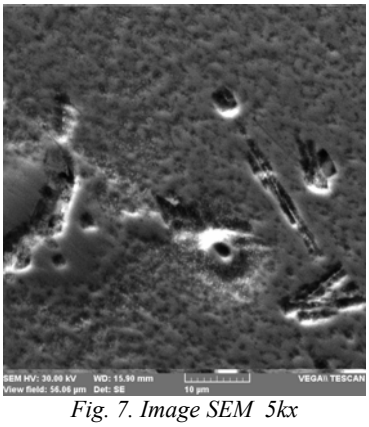
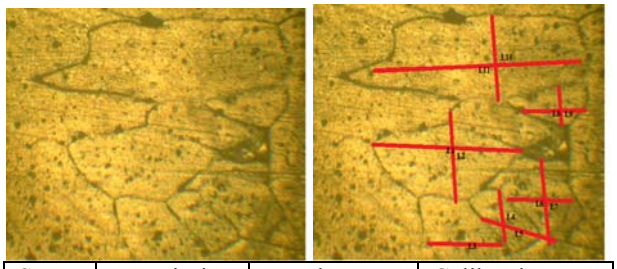


Fig. 7. Image SEM 5kx

4.2. AlFeCrMnNi optical microscopy analysis

The optical analysis of AlFeCrMnNi was performed using a X7P- 6A metallographic microscope and Materials Plus Software was used for the metallographic analysis. The following figures reveal non uniform grain sizes of the AlFeCrMnNi alloy. The samples analyzed with Materials Plus Software had a grain size of 300 µm.

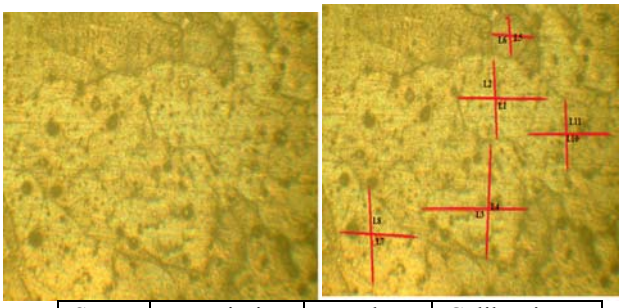
The red lines on the drawing represent grain measurements on length and width. The results of these measurements are given in the table below:



Sr.No	Description	Results	Calibration
L1	Length	526,88	X: 200/120 Y: 200/120 Micron /Pixel
L2	Length	272,08	X: 200/120 Y: 200/120 Micron /Pixel
L3	Length	255,005	X: 200/120 Y: 200/120 Micron /Pixel
L4	Length	154,236	X: 200/120 Y: 200/120 Micron /Pixel
L5	Length	240,168	X: 200/120 Y: 200/120 Micron /Pixel
L6	Length	266,51	X: 200/120 Y: 200/120 Micron /Pixel
L7	Length	231,721	X: 200/120 Y: 200/120 Micron /Pixel
L8	Length	131,93	X: 200/120 Y: 200/120 Micron /Pixel
L9	Length	228,333	X: 200/120 Y: 200/120Micron /Pixel
L10	Length	267,545	X: 200/120 Y: 200/120 Micron /Pixel
L11	Length	726,942	X: 200/120 Y: 200/120 Micron /Pixel

Fig. 8. Optical and metallographic analysis of AlFeCrMnNi alloy, grain size 300 µm.

The analysis of the AlFeCrMnNi alloy with grain size of 245 µm is presented in Fig. 9.



Sr.No	Description	Results	Calibration
L1	Length	296,671	X: 200/120 Y: 200/120 Micron/Pixel
L2	Length	223,731	X: 200/120 Y: 200/120 Micron/Pixel
L3	Length	373,337	X: 200/120 Y: 200/120 Micron/Pixel
L4	Length	315,216	X: 200/120 Y: 200/120 Micron/Pixel
L5	Length	163,639	X: 200/120 Y: 200/120 Micron/Pixel
L6	Length	116,857	X: 200/120 Y: 200/120 Micron/Pixel
L7	Length	241,948	X: 200/120 Y:200/120 Micron/Pixel
L8	Length	251,805	X: 200/120 Y: 200/120 Micron/Pixel
L9	Length	173,405	X: 200/120 Y: 200/120 Micron /Pixel
L10	Length	286,672	X: 200/120 Y: 200/120 Micron/Pixel

Fig. 9. Optical and metallographic analysis of AlFeCrMnNi alloy, grain size 245 µm.

4.3 Chemical analysis of the AlFeCrMnNi alloy

The chemical analysis was performed by EDAX. The chemical composition of the obtained alloy is given in Table 1.

Table 1. Chemical composition of the AlFeCrMnNi alloy

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Iron	26	K-series	43309	28,7578	33,30782	26,69976	0,766847
Chromium	24	K-series	38072	17,66014	20,45431	17,61067	0,535873
Manganese	25	K-series	31432	17,4699	20,23397	16,48805	0,512898
Nickel	28	K-series	12631	11,42574	13,23351	10,09362	0,328167
Aluminium	13	K-series	11134	7,719486	8,940854	14,83451	0,427655
Carbon	6	K-series	1790	3,306395	3,829529	14,27339	0,668274
			Sum:	86,33946	100	100	

A variation of the chemical elements in the AlFeCrMnNi alloy is presented in figure 10. It can be observed that Fe, Cr and Mn are the main elements in the composition of the AlFeCrMnNi alloy.

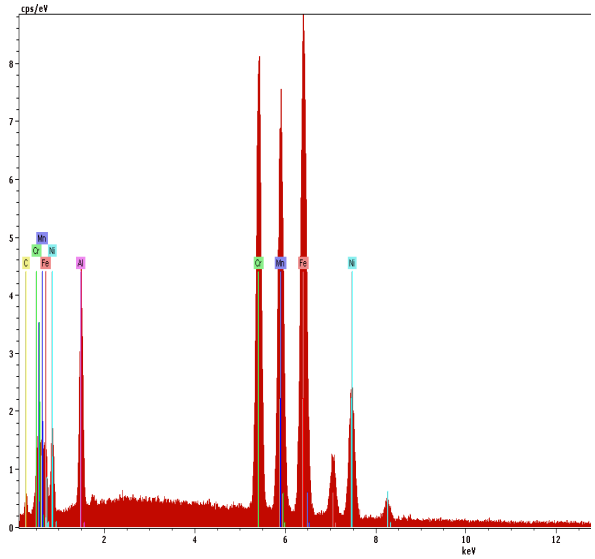


Fig. 10. Variation of chemical elements in the AlFeCrMnNi alloy.

Energy-dispersive X-ray spectroscopy also offers the possibility to analyze the chemical elements in line. The analysis was performed on an area selected from the surface of the AlFeCrMnNi alloy.

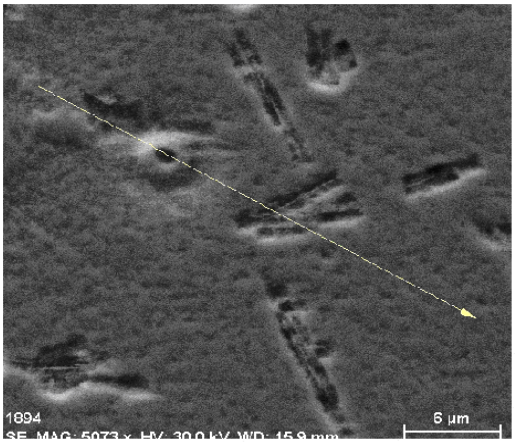


Fig. 11. Area of the AlFeCrMnNi alloy selected for chemical analysis.

Fig. 12 shows the variation of alloying elements in different points of the material for the AlFeCrMnNi alloys. The predominant elements in the AlFeCrMnNi alloy are Fe, Mn and Cr .because they have the largest quantities in this alloy.

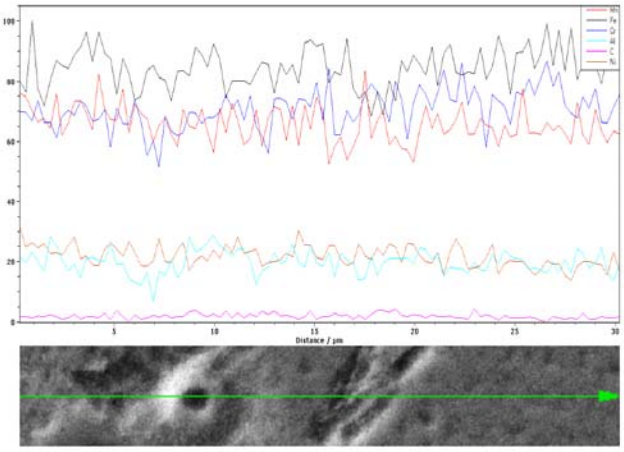


Fig. 12. In line variation of the chemical elements in the AlFeCrMnNi alloy.

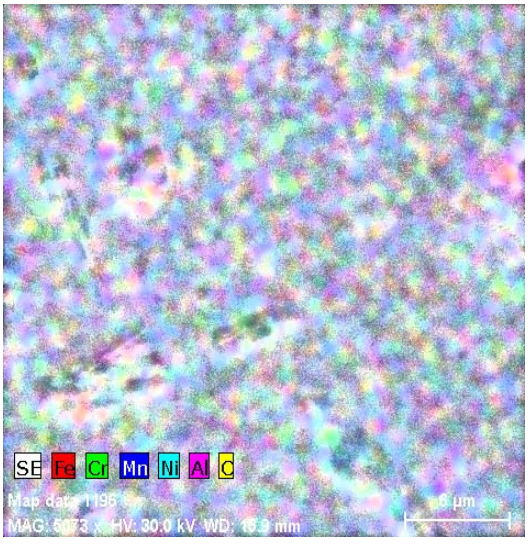


Fig. 13. Distribution of chemical elements on the surface of the AlFeCrMnNi alloy.

4.4. AlFeCrMnNi alloys microhardness

The Vickers method, standardized by STAS 492, consists in printing in a given time with a force F of an pervasive form of a quadratic pyramid square, diamond, perpendicular to test the surface and measuring the diagonal, d, of all residual prints. (see Figure 14). (Mihaela Dumitrache , 2011)

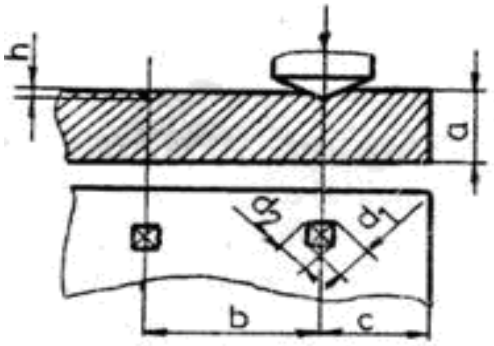


Fig. 14. Scheme of Vickers microhardness.

A PMS 73 microhardness machine was used for determining the microhardness. Microhardness results are presented in table 2. Five tests per sample were made, the penetration was performed using a penetrator type pyramid, pressing the sample with a 100g weight.

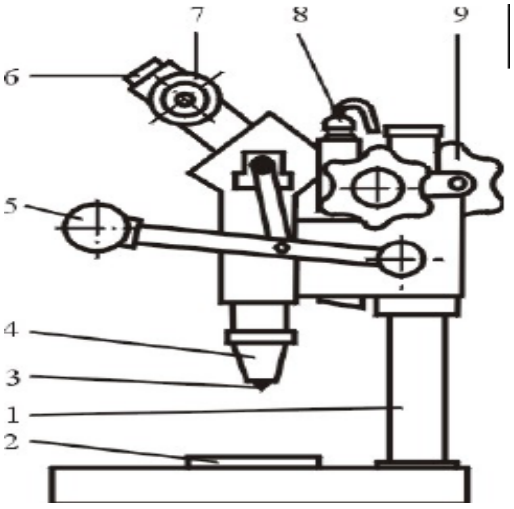


Fig. 15. Microhardness machine used to determine the Vickers microhardness for the AlFeCrMnNi alloy: 1 support column, 2 motherboard, 3 penetrator, 4 protective cone, 5 lever, 6 eye, 7 ocular micrometer , 8 light, 9 hand handle. (Mihaela Dumitrache, 2011)

The Vickers hardness (Hv) for the five tests was calculated using equation (6) ;

$$Hv = 20000 \cdot \frac{P}{N^2}, \left[daN^2/mm^2\right] \qquad (6)$$

Where: P= weight of pressing, N^2 = number of divisions.

Table 2. Microhardness values for AlFeCrMnNi alloys.

Number of attempts	P (g)	N(daN^2)	N^2(daN^2)	Hv $\left[daN^2/\right.$
1	100	64	4096	488,28
2	100	65	4225	473,37
3	100	66	4356	459,13
4	100	68	4624	432,52
5	100	69	4761	420,07

4.5 Rockwell hardness of the AlFeCrMnNi alloy

The hardness is the ability of an object to resist the tendency of the superficial layers to be destroyed by another object and the pressure acting on its surface on very small areas and to not obtain permanent deformations (Mihaela Dumitrache 2011).

The method consists in printing a Rockwell penetrator (diamond cone or steel bile) with an initial load with overload F0 and F1 and then measuring the depth of penetration in material, after removal of overload, maintaining the initial load applied (Figure 16) (Mihaela Dumitrache, 2011).

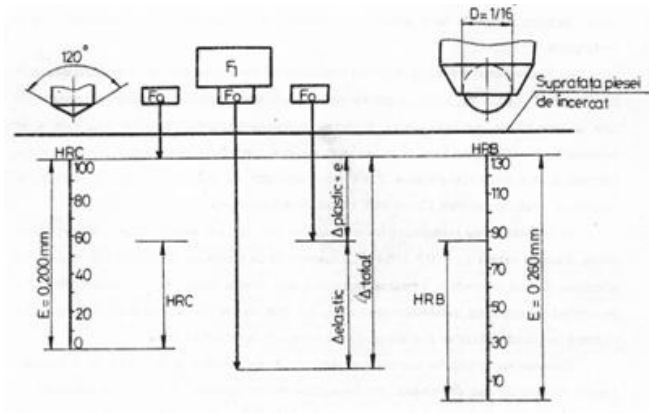


Fig. 16. The scheme of the Rockwell hardness test.

To determine the Rockwell hardness of the AlFeCrMnNi alloy Wilson Wolpert 751 N universal hardness machine was used with a pressing weight was 150 kg. Three tests were made on the AlFeCrMnNi alloys surface and from the results it can be observed that the material has a high hardness. The obtained values are presented in Table 3.

Table 3. Values of the Rockwell hardness for the AlFeCrMnNi alloy.

Number of trial	Rockwell hardness values
1	52.10 HRC
2	54,61 HRC
3	54,29 HRC

4.6 X-ray Diffraction alloy AlFeCrMnNi

The X-ray diffraction is a non-destructive analytical technique used to identify and quantitatively determine various crystalline compounds, known as "phases", compounds that are present in solids and powders.

The X-ray analysis was performed using an PANalytical X'Pert PRO MPD Diffractometer on the AlFeCrMnNi alloy. Fig. 17 shows the results of the analysis.

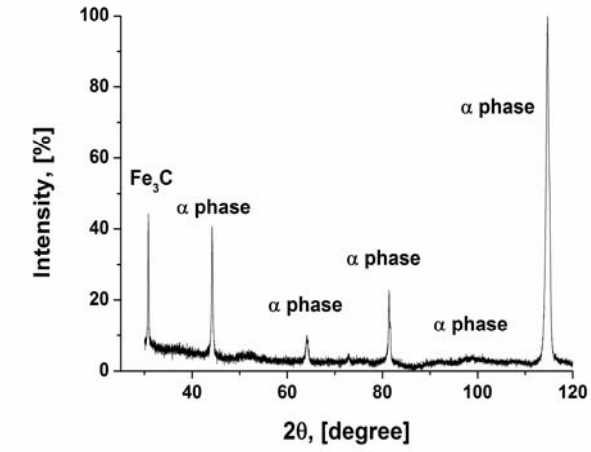


Fig. 17. Diffractogram of the AlFeCrMnNi alloy

After the analysis, it can be observed that some intermetallic compounds are formed in the structure of the AlFeCrMnNi alloy. Also, at a 50% intensity, cementite and α phases are possible combinations of Fe with the other alloying elements in the studied material.

5. Conclusions

From the analysis performed on the AlFeCrMnNi alloy it was found that this alloy has a high hardness. so the results observed in the microhardness and hardness.

Analyzing the AlFeCrMnNi alloy by scanning electron microscopy it was observed that the alloy has a FCC structure and exhibits a dendritic morphology after the solidification process.

After casting, the final chemical composition of the alloy is similar to the elaborated alloy.

After X-ray analysis it was observed that the structure of the AlFeCrMnNi alloy contains some intermetallic compounds.

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