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Processing and characterization of advanced multi-element high entropy materials from AlCrFeCoNi system

V. GEANTĂ[a], I. VOICULESCU[a], R. ŞTEFĂNOIU[a,*], D. SAVASTRU[b], I. CSAKI[a], D. PATROI[c], L. LEONAT[c]
[a]*POLITEHNICA University of Bucharest, 313 Splaiul Independenţei, 060042, Bucharest, Romania*
[b]*National Institute for Research and Development in Optoelectronics-INOE 2000, 409 Atomistilor str. Magurele, Romania*
[c]*ICPE-CA, Splaiul Unirii, nr.313, sect.3, Bucharest, Romania*

The multi-element materials with high entropy, generic called High Entropy Alloys - HEA, contains at least five metal elements, at concentrations between 5 and 35 atomic %. Recent researches in the field has shown that such materials have superior properties compared to traditional alloys (steel, super alloys etc.), and therefore, can be used in the top fields of the industry. High entropy alloys can be designed to have special characteristics such as high hardness combined with toughness and plasticity, which can be influenced by the chemical composition. The paper presents the results regarding the processing and characterization of high entropy multi-element materials from as cast AlCrFeCoNi class, for which were studied the influence of chemical composition on the mechanical and structural properties. It was found that by fast cooling of HEA, the breaking energy values are in the range 60 ... 72 J, while the microhardness varies in the range of 169…516 $HV_{0.1}$, depending on the materials composition.

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1. Introduction

Traditional alloys use one metallic element representing base matrix (denominated solvent element, as iron, aluminium, copper, titanium, magnesium etc) in which are introduced, in different percentages other alloying elements (dissolved elements) to obtain secondary phases. Traditional metallurgical theory suggests that multiple alloying elements in an alloy may lead to the formation of many compounds with complex microstructure and poor mechanical properties [1, 14]. Recently, this paradigm has been broken by high entropy alloy developed by Yeh et al. [1].

New class of multi-element alloys appeared from chemical combination being characterized by superior properties in comparison to classical alloys. A new concept in metallic materials processing was the foundation for producing these advanced multi-element materials. These materials were named “high entropy alloys”, due to the higher mixing entropies at atomic scale than the traditional alloys in liquid state or solid solutions [1, 2, 3, 4, 5].

High entropy alloys (HEA) consists in “n” elements ($n \geq 5$) introduced in equimolar or nearly equimolar ratios resulting in formation of solid solution phases, nanostructures or amorphous phases in as-cast state [6, 7, 8]. High entropy alloys are solid solution with improved resistance, good thermal stability and quenching capacity higher than classical alloys combined with high resistance capacity in different environments [9, 10, 11, 12]. The high atomic disorder degree results in unique variations at sub-microscopic scale, which determines the obtaining of special mechanical properties (hardness, wear resistance) or electrochemical properties (oxidation and corrosion resistance).

High entropy alloys microstructure is practically “frozen” at the melt level, embedding in solution a very different chemical elements conglomerate (iron related elements like Cr, Ni, Co, which form solid solutions, together with Al, a transitional metal with different solubility in Fe, Cr, Ni and Co). This joining creates entropy with high values and explains the obtainment of different characteristics than alloy cooled with usual rates. One or two solid solutions are formed function of alloying elements percentage embedding the other alloying elements. The dendrites microstructure is dominant and needle compounds or spheroidal precipitates can be observed function of chemical composition and cooling rate.

The chemical elements association in the alloy network is determined by the reciprocal chemical affinity and the solid solution formation tendency (b.c.c. or f.c.c.) with solubility dependent on atomic proportion of each element. The excess element in a solid solution type can be dissolved in the other compatible element matrix (e.g. Co and Ni forms a continuous solid solution (CoαNi) but can also dissolve in Fe stabilizing the austenite; for 17%Fe in Co, Feδ can be found; solubility of Co in Cr is high (approx 12% Co) at ambient temperature and solubility of Cr in Co is appreciable) [12]. For advanced consolidating effect, elements forming hard compounds can be added (e.g. eutectics Al_2Fe, Al_5Fe_2, $AlFe_3$) but does not determine the brittleness due to the fact that the compounds are embedded in a tough matrix with stable and strong interfaces.

Alloys from AlCrFeCoNi class have a high compression resistance, yield and tension resistance, measured values being 2004 MPa, 1250MPa and respectively 32.7 % [13, 14, 15]. More, the cooling rate increasing contribute to increasing of plasticity and resistance due to chromium segregation effect decreasing and grain refining effect [16 - 23].

The paper presents results regarding the processing and characterization of high entropy multi-element materials from AlCrFeCoNi class and the influence of chemical composition on the mechanical and structural properties. The characterization consisted in microhardness measurement, Charpy tests and microstructure analysis by optical and scanning electron microscopy. The analysis of chemical composition has been done using X-ray fluorescence spectrometer.

2. Experimental procedure

One of the usual method for obtainment of high entropy alloys is electric arc melting of the charge in vacuum arc remelting installation (with current values till 500A), in controlled atmosphere (VAR). Alloy ingot with nominal composition of AlxCrFeCoNi (x: atomic ratio, x= 0.2; 0.6; 0.8; 1.4) were obtained using arc melt casting in a vacuum arc remelting installation (MRF ABJ 900), placed in Laboratory ERAMET - Materials Science and Engineering Faculty from Politehnica University of Bucharest.

The maximum level for preliminary vacuum was obtained with diffusion pumps at 10^{-5} mbar and high – purity argon atmosphere was used as feeding gas system. The samples were melted in electric arc through tungsten electrode (Φ 6.5 mm) and tungsten pin placed on double wall water cooled copper base plate.

For experiments was considered four different compositions of high entropy alloys, varying the quantity of some elements considered with an important influence on the mechanical properties. The experimental charges had the following chemical configuration:

HEA 5 – $Al_{0.8}CrFeCoNi$;
HEA 6 – $Al_{0.6}CrFeCoNi$;
HEA 8 – $Al_{0.2}CrFeCoNi$;
HEA 10 – $Al_{1.4}CrFeCoNi$.

Raw materials used for producing the experimental samples have advanced purity (99.8%) and were selected according to the chemical composition and particle-size analysis point of view in order to be proper placed in the cavities of the water cooled copper plate. For metallic charge calculus were taken into account the theoretical assimilation degrees and eventual losses by vaporization during metallurgical processes in vacuum or in high purity argon atmosphere. The losses are extremely low due to the fact that the charge is very clean and the experiments were developed in vacuum atmosphere and argon, and the short processing time limit to the maximum losses due to evaporation during electric arc processing. To improve the chemical homogeneity, the ingots were remelted for 5 to 7 times with successive turning on opposite side.

3. Results and discussion

3.1. Microhardness

The microhardness was determined by Vickers hardness instrument. Vickers' load was 980.7 mN with a loading time of 10 s, using a Shimadzu HMV 2TE microhardness tester. The microhardness values was measured on the polished surfaces of samples HEA 5, HEA 6, HEA 8 and HEA 10, and are shown in Table 1.

Table 1. Microhardness values, $HV_{0.1}$.

Sample	**HEA 5**	**HEA 6**	**HEA 8**	**HEA 10**
1	273	249	161	495
2	309	256	165	528
3	295	241	167	511
4	303	250	165	510
5	296	233	187	539
Average	**295.2**	**245.8**	**169**	**516.6**

It can be observed that the hardness of AlCrFeCoNi class high entropy alloys decrease proportionally with the aluminium content decreasing from 516.6 $HV_{0.1}$ for HEA 10 (with the maximum content of Al – 1.4) to 169 $HV_{0.1}$ for HEA 8 (with the minimum content of Al – 0.2). The hardness decreasing could be explained by reducing the quantity and number of hard precipitates (Fe-Al compounds) in metallic matrix.

3.2. Toughness

The Charpy V-notch impact tests were performed on a Charpy pendulum at room temperature, measuring the values of energy absorbed in the process of dynamic fracture by a standardized notched sub-size specimen (5×10×60 mm). The obtained values are shown in Table 2.

Table 2. Values for breaking energy in Charpy test, J.

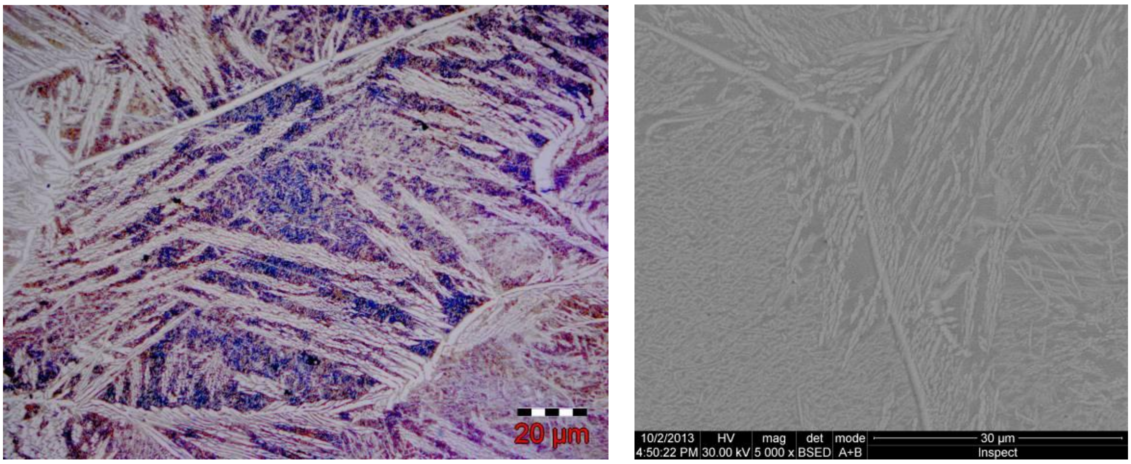
Sample	**HEA 5**	**HEA 6**	**HEA 8**	**HEA 10**
1	62.4	67.0	71.2	60.1
2	62.3	66.9	73.0	61.2
3	62.1	67.1	72.4	60.6
4	62.1	68.9	72.2	60.2
Average	**62.22**	**67.47**	**72.2**	**60.52**

The fracture energy value is in the 60…72 J intervals for all of the four types of alloy, with hardness oscillating between 169…516 $HV_{0.1}$. As a direct consequence the hardening effect will not decrease significant the metallic matrix tenacity in the case of analyzed high entropy alloys.

3.3. Microstructure

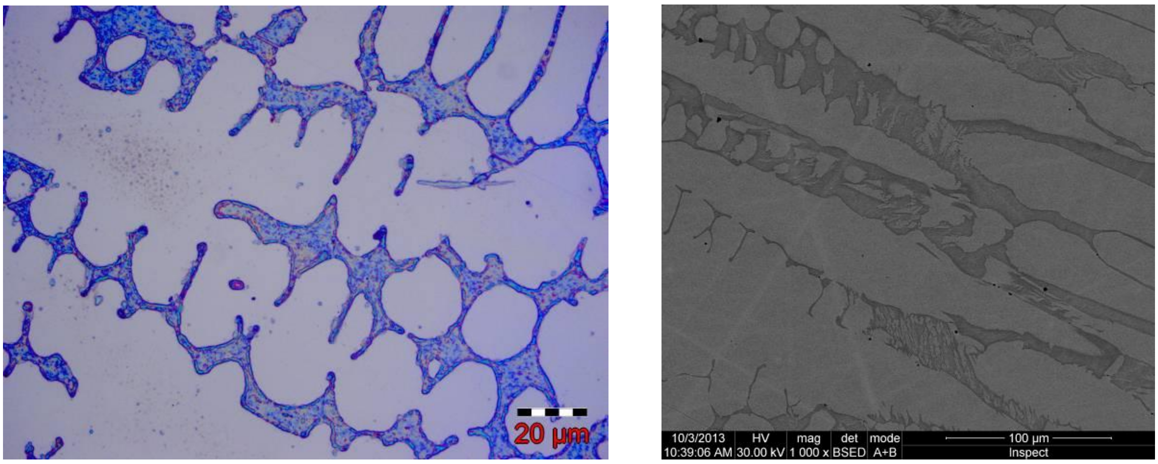
The microstructures obtained by optical and electronically microscopies are shown in Figs. 1 – 4.

The metallographic samples of HEA were obtained using a precise cutting machine IsoMet 4000, were mechanically wet ground using a 600, 800, 1000 and 2400 SiC grit paper and then were polished with Al_2O_3 powder of 1 and 0,6 µm diameter.



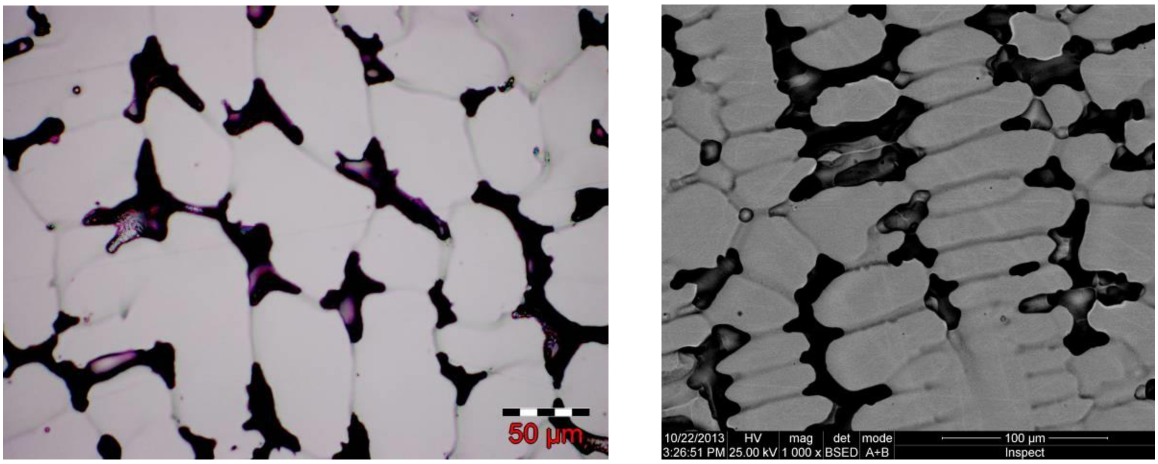
a) 1000x b) 5000x

Fig. 1. Microstructure of ***HEA5 (****Al* $_{0.8}$ *CrFeCoNi****)*** *alloy: a) optical image; b) SEM backscattered electron image.*



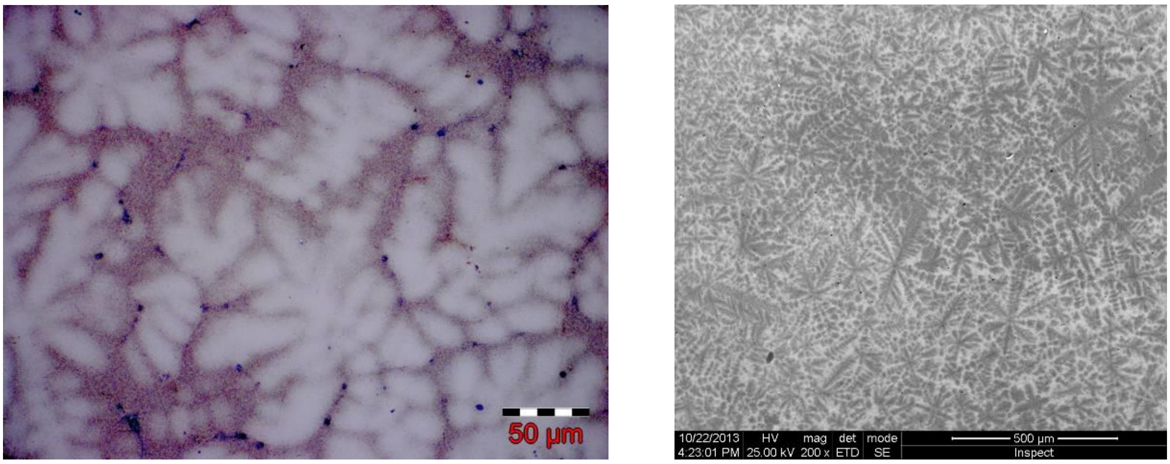
a) 1000 x b) 1000 x

Fig. 2. Microstructure of ***HEA 6 (****$Al_{0.6}$CrFeCoNi****)*** *alloy: a) optical image; b) SEM backscattered electron image.*



a) 500 x b) 1000 x

Fig. 3. Microstructure of ***HEA 8 ($Al_{0.2}$CrFeCoNi)*** *alloy: a) optical image; b) SEM backscattered electron image.*



a) 500 x b) 200 x

Fig. 4. Microstructure of ***HEA 10 ($Al_{1.4}$ CrFeCoNi)*** *alloy: a) optical image; b) SEM electron image.*

The etching was done for 30 seconds in 10% oxalic acid at 24°C. After etching the samples was cleaned with distilled water and ethanol, and then dried in hot air. Subsequently, the high entropy alloys was examined by optical microscopy (using an optic microscope Olympus GX 51) and by scanning electron microscopy, using a Inspect S SEM microscope. Depending on chemical composition of the metallic alloys, the microstructure aspects shows specific particularities.

Thus, the optical microscopy indicates for HEA 5 (Fig. 1) polyhedral grains formation and a needle-like phase that grow from the grain boundaries. Regarding HEA 6, microstructure contains dendrites and inter-dendrites precipitate (Fig. 2). In the case of HEA 8 (Fig. 3) it can be observed the coarse and oriented dendrite formations and fine inter-dendrites precipitates. For HEA 10 (Fig. 4) the microstructure contains dendrites and intermetallic precipitates.

The analysis of multi-element in solid samples, with detection range from ppm to 100%, has been done using X-ray fluorescence spectrometer by wavelength (WDXRF) tip S8 TIGER 1 KW – Bruker (Table 3 and Fig. 5 - 7).

Table 3. Composition analysis (EDS) of high-entropy alloys.

Alloy	Element	Concentration	Line 1	Net int.	Stat. error	LLD	Analyzed layer
HEA 5	Co	23,70 %	Co KA1-HR-Tr	857,9	0,193 %	163,3 PPM	16,1 um
	Fe	23,67 %	Fe KA1-HR-Tr	699,5	0,214 %	140,3 PPM	13,2 um
	Ni	20,48 %	Ni KA1-HR-Tr	180,3	0,422 %	238,7 PPM	12,0 um
	Cr	20,21 %	Cr KA1-HR-Tr	620,7	0,227 %	99,4 PPM	18,0 um
	Al	**11,69 %**	Al KA1-HR-Tr	40,65	0,891 %	234,0 PPM	0,67 um
HEA6	Fe	26,49 %	Fe KA1-HR-Tr	796,3	0,201 %	135,8 PPM	12,8 um
	Co	25,09 %	Co KA1-HR-Tr	923,4	0,186 %	164,4 PPM	15,7 um
	Ni	21,23 %	Ni KA1-HR-Tr	184,6	0,417 %	250,8 PPM	11,1 um
	Cr	20,01 %	Cr KA1-HR-Tr	634,7	0,225 %	109,6 PPM	17,5 um
	Al	**6,89 %**	Al KA1-HR-Tr	23,82	1,17 %	226,0 PPM	0,62 um
HEA8	Fe	26,97 %	Fe KA1-HR-Tr	776,9	0,203 %	153,0 PPM	11,8 um
	Co	25,80 %	Co KA1-HR-Tr	909,4	0,188 %	179,6 PPM	14,4 um
	Cr	22,55 %	Cr KA1-HR-Tr	711,0	0,212 %	110,4 PPM	17,5 um
	Ni	22,11 %	Ni KA1-HR-Tr	186,0	0,415 %	259,8 PPM	10,3 um
	Al	**2,44 %**	Al KA1-HR-Tr	8,276	1,98 %	145,6 PPM	0,58 um
HEA 10	**Al**	**43,52 %**	Al KA1-HR-Tr	194,4	0,407 %	303,0 PPM	1,29 um
	Fe	14,99 %	Fe KA1-HR-Tr	512,6	0,250 %	95,4 PPM	19,6 um
	Cr	14,21 %	Cr KA1-HR-Tr	412,9	0,279 %	85,1 PPM	21,5 um
	Co	14,04 %	Co KA1-HR-Tr	606,5	0,230 %	112,9 PPM	24,2 um
	Ni	12,69 %	Ni KA1-HR-Tr	141,6	0,476 %	162,8 PPM	20,2 um

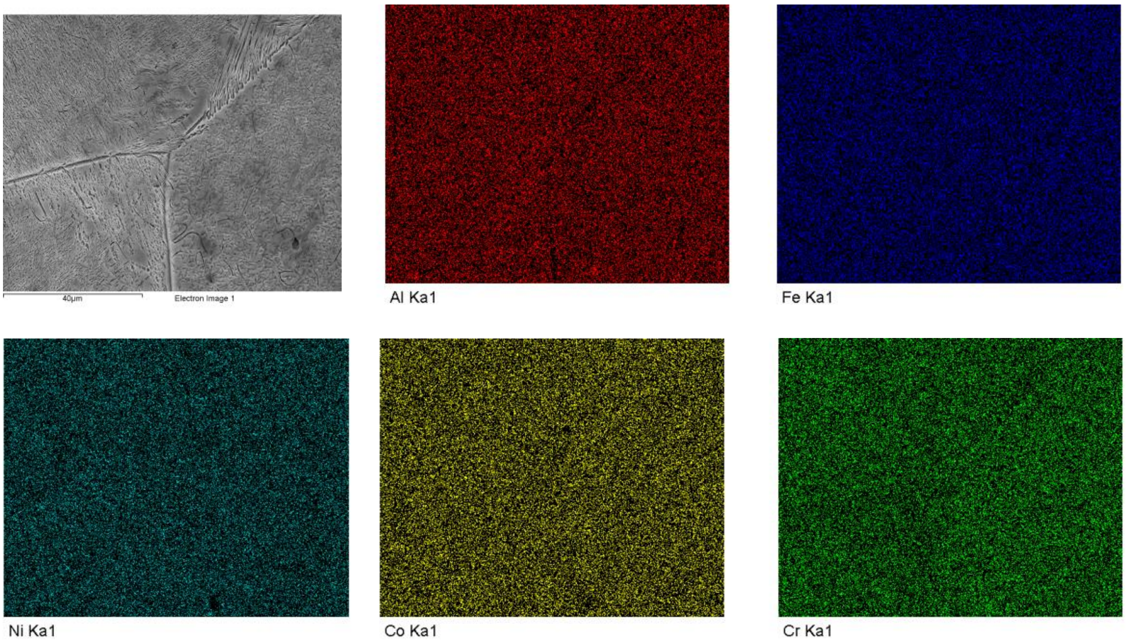


*Fig. 5. SEM microscopy of **HEA 5 ($Al_{0.8}CrFeCoNi$)** alloy. Polyhedral grains of solid solution and distribution of chemical elements.*

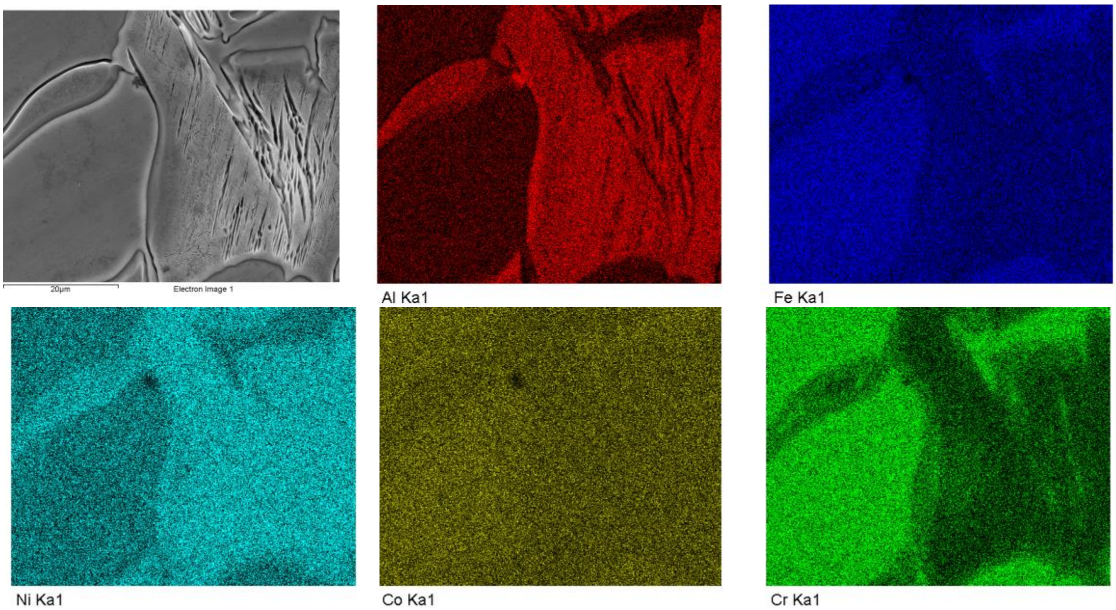


*Fig. 6. SEM Microscopy of **HEA 6 ($Al_{0.6}CrFeCoNi$)** alloy. Dendrites (Cr, Co and Fe) and distribution of other chemical elements into the interdendritic area (Ni, Al).*

As can be seen in Fig. 5 (HEA 5), microstructure contains polyhedral grains, with grain boundaries well defined, and distribution of components in the metal matrix is almost uniform. By reducing the percentage of aluminium participation from 0.8 to 0.6 (HEA 6, Fig. 6) and then to 0.2 (HEA 8, Fig. 7) appears a tendency to separate the elements in the alloy with high entropy, into interdendritic zone (preponderantly Al and Ni) and the formation of homogeneous solid solutions into the dendrites (Fe, Cr). This behaviour is dictated on the one hand, by the lower values of the melting temperatures of Al and Ni compared to other elements involved and, on the other hand, by the trend of forming solid solutions between combinations of elements.

For the three described cases, cobalt is distributed uniformly in the metallic matrix, regardless of the percentage of aluminium in alloy, because it has sufficient mutual solubility with Cr and Ni.

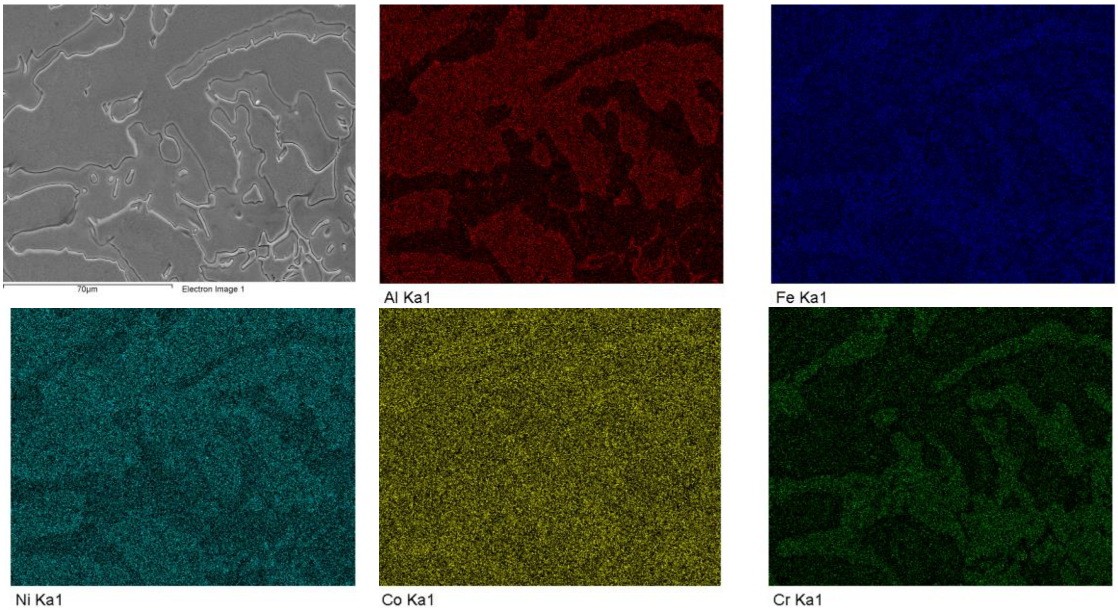


*Fig. 7. SEM microscopy of **HEA 8 ($Al_{0.2}CrFeCoNi$)** alloy. Dendrites and distribution of main chemical elements.*

3. Conclusions

The microhardness values of the obtained alloys are approximately two times higher than the one obtained for classical alloys (e.g. carbon steel). From experimental data analysis result that on each sample exist a quasi constant microhardness value proving the good homogeneity of samples obtained in VAR equipment. The alloying elements influence is observed due to the wide hardness values interval.

The fracture energy is in the 62…72J interval with hardness oscillating between 169…516 $HV_{0.1}$. As a direct consequence, the hardening effect will not decrease the metallic matrix tenacity in the case of analyzed high entropy alloys.

High entropy alloys microstructure is practically "frozen" at the melt level, embedding in solution a very different chemical elements conglomerate. This creates high value entropy and explains the achievement of different characteristics than the alloy cooled with usual rates. One or two solid solutions are formed function of alloying elements percentage embedding the other alloying elements. The dendrites microstructure is dominant and needle-like or spherical compounds can be observed function of chemical composition and cooling rate.

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*Corresponding author: radustefanoiu@yahoo.com