

Chemical Composition Influence on Microhardness, Microstructure and Phase Morphology of Al_xCrFeCoNi High Entropy Alloys

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The AlCrFeCoNi high entropy alloy exhibits unexpected properties that can be obtained after mixing five different elements, which could not be obtained from any one independent element. The difference to conventional alloys is that these alloys may have, at the same time, both hardness and plasticity, can be used in severe impact applications. In order to study the influence of aluminum content on the microhardness and microstructure of the high entropy alloys Al_xCrFeCoNi (x: atomic ratio, x= 0.2 to 2.0) nine types of samples were obtained as mini-sized ingots (50x15x9.5 mm and 40 g weight). The mini-ingots were obtained using arc melt casting process in a vacuum arc remelting device (VAR MRF ABJ 900). The influence of the chemical elements on the microstructure, phases morphology and microhardness of Al_xCrFeCoNi system was studied. The results have confirmed that mechanical properties could be greatly adjusted by the chemical composition change. The main element that influences the microhardness of the analyzed system is aluminum, due to the formation of Al-Fe compounds with high hardness. Increasing the aluminum content in the alloy to values greater than 1.8 ... 2 at.% contribute to the increase of hardness and also to the embrittlement thereof. Other elements like Cr, Fe, Co and Ni can contribute to mitigate increasing the hardness of the alloy. The type of phases formed in high entropy alloy are dependent to the aluminum concentration. So, depending on of aluminium content, different phases are obtained, like FCC for low Al content, mixture of FCC and BCC for about 2.5 %Al and BCC for high Al content. The crystallite size depends on the chemical composition and increase with the aluminium content.

Keywords: high entropy alloys, microhardness, microstructure, phases morphology

High Entropy Alloys (HEA) are composed of major alloy elements with $n \geq 5$ in equi-molar or near equi-molar ratio, which yields easier the formation of simple FCC or BCC solid solution phase, with nano-structure or amorphous structure, in as-cast state [1]. These alloys can include numerous principal elements in equimolar or near-equimolar ratios, each varying in the range of 5 - 35 at. % [2, 3]. Therefore, many researches related to HEAs report that these alloys show high strength (both at room temperature and in cryogenic conditions), good thermal stability and large work hardening capacity, greater fatigue ratio than the materials with comparable tensile strengths, good wear resistance, corrosion resistance at ambient temperature superior to that of 304 stainless steels [4]. If a solid solution is kept, the alloy would have a better combination of strength and plastic deformation behavior. By increasing of alloying elements content, some intermetallic compounds are typically formed, due to the limited mutual solubility with the main chemical element of solid solution. That leads to hardening of metallic matrix, but also leads to embrittlement. To obtain a solid solution structure, a new design concept for metallic alloys has been proposed, like multi-element alloy or high-entropy (HE) alloy [Yeh et al.] based on the thermodynamic principle, which consists of a simple FCC or BCC structure [5- 7]. If the chemical composition of the alloy is well designed, intermetallic compounds are absent and a single

solid solution is built, having different type of phases: single FCC, single BCC or FCC + BCC mixture. In such conditions, mechanical and microstructural characteristics of HE alloys are equilibrated, the metallic matrix being ductile and hardenable, having high strength up to 800°C [6-10].

Many high entropy alloy systems have been investigated in the past decade, such as: AlCoCrCuFeNi [1, 3, 11, 12, 19], FeNiCrCuCo and FeNiCrCuMo [2], AlTiVCrMnFeCoNiCu, CoCrFeNiTiAl, CuNiCoZnAlTi, AlCoCrCuNi, AlFeTiCrZnCuNi, AlCrFeMnNi, VCrMnMoW [4], AlCrFeMnNi [5, 10], AlCrFeCoNi [6-9, 13-15, 17, 20-26]. Mechanical properties and microstructure of these alloys have been studied and reported extensively in the literature [7 - 27]. The carbides and nitrides of HEAs can be used as coatings for the biomedical materials [4]. Due to its excellent mechanical properties (yield stress of 1250.96, MPa compressive strength of 2004.23 MPa and plastic strain of 32.7%) AlCrFeCoNi alloy can be used also for severe impact applications [10 - 12]. The excellent high-temperature properties can be an advantage of HEAs to replace the Ni-based superalloy, e.g., AlCoCrFeNi, having lighter weight and a lower cost. HEAs has excellent wear resistance and can be used for hardfacing of mold materials [20, 21].

In the paper, the influence of aluminium on the microstructure, phase's morphology and hardness of Al_xCrFeCoNi have been studied. By increasing of the aluminium content, microhardness has increase from 169

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Table 1
CHEMICAL COMPOSITION OF THE $Al_xCrFeCoNi$ SAMPLES

Alloy	Chemical composition									
	Al		Cr		Fe		Co		Ni	
	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %
HEA 1 - $AlCrFeCoNi$	20	10.67	20	20.55	20	22.13	20	23.33	20	23.32
HEA 2 - $Al_{1.5}CrFeCoNi$	27.28	15.2	18.18	19.51	18.18	21.01	18.18	22.14	18.18	22.14
HEA 3 - $Al_2CrFeCoNi$	33.36	19.28	16.66	18.57	16.66	20	16.66	21.08	16.66	21.07
HEA 5 - $Al_{0.8}CrFeCoNi$	16.68	8.72	20.83	21.00	20.83	22.62	20.83	23.83	20.83	23.83
HEA 6 - $Al_{0.6}CrFeCoNi$	13.04	6.69	21.74	21.47	21.74	23.12	21.74	24.36	21.74	24.36
HEA 7 - $Al_{0.4}CrFeCoNi$	9.12	4.56	22.72	21.96	22.72	23.66	22.72	24.91	22.72	24.91
HEA 8 - $Al_{0.2}CrFeCoNi$	4.76	2.33	23.81	22.47	23.81	24.2	23.81	25.5	23.81	25.5
HEA 9 - $Al_{1.2}CrFeCoNi$	23.08	12.54	19.23	20.12	19.23	21.68	19.23	22.83	19.23	22.83
HEA 10 - $Al_{1.4}CrFeCoNi$	25.96	14.32	18.51	19.71	18.51	21.22	18.51	22.37	18.51	22.37

to 589HV_{0.1}, and crystallite size has increase from 20.13nm to 43.10 nm. In as-cast state, metallic matrix has dendritic microstructure and ductile-fragile fracture mode. Next studies will be dedicated to the influence of the heat treatments on the mechanical properties and microstructure.

Experimental part

The method used to prepare high entropy alloys was the electric arc melting of the raw metallic components in vacuum arc remelting installation, by keeping under control of the working atmosphere (Vacuum arc remelting - VAR, type MRF ABJ 900, in ERAMET Laboratory of Materials Science and Engineering Faculty from Polytechnic University of Bucharest). During the melting process, high purity argon atmosphere was used for ignition of the electric arc and for protecting the melted alloy. The level of oxygen content in the vacuum chamber was 60 ppm. The raw materials (with advanced purity more than 99.8%) were: ARMCO iron, metallic Cr, electrolytic Ni, metallic Co and Al. For calculus of ingot volume, were taken into account the theoretical assimilation degrees and eventual losses by vaporization during metallurgical processes in vacuum or in high purity argon atmosphere. According to previous results of the research team [8,9, 20, 22], the losses were extremely low due to the fact that the row materials have been properly selected and cleaned, and the experiments were developed in vacuum and argon atmosphere. During melting, very short processing time allows to avoid the massive losses due to evaporation during electric arc processing. To improve the chemical homogeneity, the ingots were remelted 5 to 7 times with successive turning and remelting on opposite side. To study the influence of aluminum content on the micro-hardness and microstructure nine different $Al_xCrFeCoNi$ alloy were prepared (x : atomic ratio, $x=0.2$ to 2.0), as mini-sized ingots with 50x15x9.5 mm dimensions and about 40 g weight each. The chemical composition of experimental samples is presented in table 1.

Results and discussions

Microhardness $HV_{0.1}$

The micro-hardness has been measured on the polished surfaces, using a Shimadzu HMV 2TE Vickers hardness

apparatus, using load of 980.7 mN and measuring time of 10 s. The average microhardness values obtained for the HEA's alloys are: HEA 1 - $AlCrFeCoNi$ ($x=1$) $HV_{0.1} = 562.6$; HEA 2 - $Al_{1.5}CrFeCoNi$ ($x=1.5$), $HV_{0.1} = 533.8$; HEA 3 - $Al_2CrFeCoNi$ ($x=2$), $HV_{0.1} = 589.6$; HEA 5 - $Al_{0.8}CrFeCoNi$ ($x=0.8$), $HV_{0.1} = 427$; HEA 6 - $Al_{0.6}CrFeCoNi$ ($x=0.6$), $HV_{0.1} = 245.8$; HEA 7 - $Al_{0.4}CrFeCoNi$ ($x=0.4$), $HV_{0.1} = 179.2$; HEA 8 - $Al_{0.2}CrFeCoNi$ ($x=0.2$), $HV_{0.1} = 169$; HEA 9 - $Al_{1.2}CrFeCoNi$ ($x=1.2$), $HV_{0.1} = 530.6$; HEA 10 - $Al_{1.4}CrFeCoNi$ ($x=1.4$), $HV_{0.1} = 516.6$. The microhardness values were used to analyze the influence of chemical elements (Al, Cr, Fe, Co and Ni) on the metallic matrix hardening (figures 1 to 4). The influence of each chemical element on the amplitude of hardening effect was analyzed using a statistical program, and the contribution of each item was represented through a simple linear distribution. During data processing has been taken into account the following assumptions: the areas analyzed from the samples were

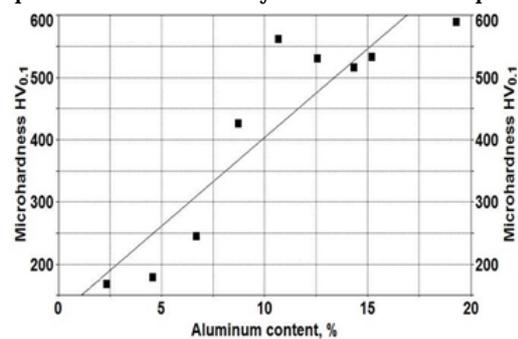


Fig. 1. Influence of aluminum content on the microhardness $HV_{0.1}$.

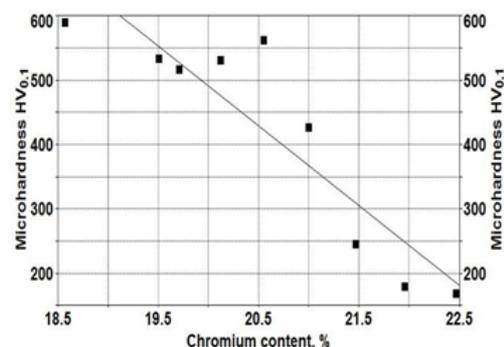


Fig. 2. Influence of chromium content on the microhardness $HV_{0.1}$.

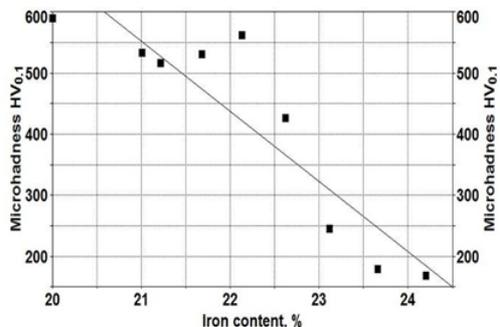


Fig. 3. Influence of iron content on the microhardness $HV_{0.1}$.

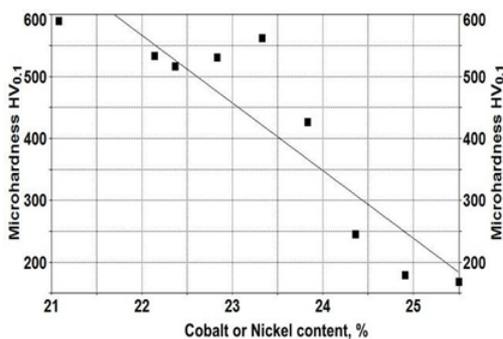


Fig. 4. Influence of cobalt/nickel content on the microhardness $HV_{0.1}$.

approximately equal distributed; the measurements values of each sample were independent; the variances of the points in the analyzed area were equal. For the maximum content of aluminum in HEA 3 - $Al_2CrFeCoNi$ ($x=2$), has been obtained the maximum value of microhardness ($HV_{0.1} = 589.6$). The other chemical elements (Ni, Cr, Co, Fe) tend to cause a reduction in hardness, with increasing their content in the alloy. The effects of Ni and Co was analyzed together (fig. 4), due to their similar influence on the matrix hardening.

Microstructural analysis

The samples obtained by cross section of the mini-ingots were hot mounted in Bakelite and prepared for metallographic analysis in accordance with the metallographic sample preparation procedure of LAMET laboratory from UPB [9, 20]. After that, samples were

electrochemically etched in 10% oxalic acid solution to reveal structural details by preferential attack of metal surface. The prepared surfaces were examined by optical microscopy (fig. 5). HEA 1 fracture surfaces have been examined by electron microscopy SEM (fig. 6). For all samples, the microstructure of casted samples shows dendritic formations and very thin inter-dendritically regions. Microstructures of $Al_{0.8}CrFeCoNi$ and $Al_{1.4}CrFeCoNi$ samples are composed of oriented dendrites, evenly distributed, which stop in a very precise manner on common interfaces. Fracture surfaces expresses the specific features of microstructure, emphasizing cleavage fracture mode, with sliding planes and mixed areas of ductile fracture.

To identify the phase compounds of the $AlCrFeCoNi$ alloys, a Panalytical X'Pert Pro MPD X-ray diffractometer with $Cu K_{\alpha}$ radiation (1.54060 [Å]), with the following parameters: $\theta-2\theta$: 20-100°, step size (°): 0.01313, time per step (s): 60, scan speed: (°/s): 0.0547 and number of steps: 6093, was used. Structures of (HEA1- HEA10) alloys were examined using XRD method and the results are presented in the figure 7. In all cases FCC phase is observed. There appears to be only one group of diffraction peaks in HEA 7 and HEA8, which it corresponds to β -type - FCC phase (minimum content of aluminum). Similarly, a group of X-ray peaks in HEA1, HEA2, HEA3, HEA5, HEA6, HEA9, and HEA10 respectively, which corresponds to both α -type - BCC phase and FCC phase. This findings stay in line with results obtained by Chen [13], Lin [14], Jasiewicz [16] and D'brova [17]. The strengthening of FCC phase is highlighted by formation of the $AlFe$ and Al_2Fe compounds at 2θ angle of 44.169°, respectively 81.332° and also the appearance of $AlCrFe$ compound with predominant peak at 2θ angle of 64.355°. Increasing the concentration of aluminum leads to FCC phase transition towards BCC phase, highlighted with a transition zone around HEA6 concentration, which has a biphasic structure (FCC + BCC). This is in concordance with micro-hardness values, FCC phase being less hard than BCC phase.

Crystallite sizes were determined using the Scherrer equation [15], using the full width of the diffraction line. The values measured it is located in the range of 20.13 ~ 40.41 nm (table 2). As result of the determined values for the average size of crystallites, for maximum

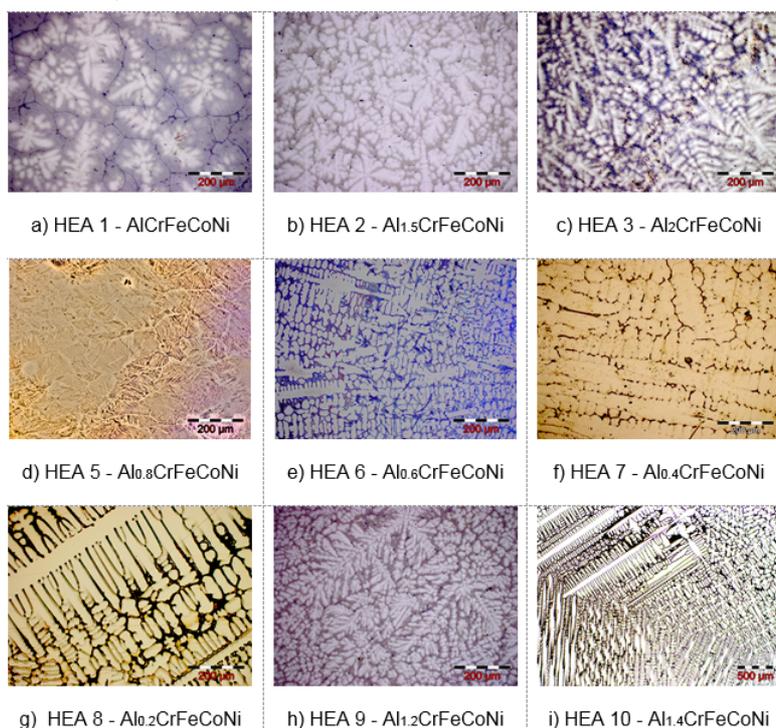


Fig. 5. Microstructure of $Al_xCrFeCoNi$ in as-cast condition: a) $x=1$; b) $x=1.5$; c) $x=2$; d) $x=0.8$; e) $x=0.6$; f) $x=0.4$; g) $x=0.2$; h) $x=1.2$; i) $x=1.4$

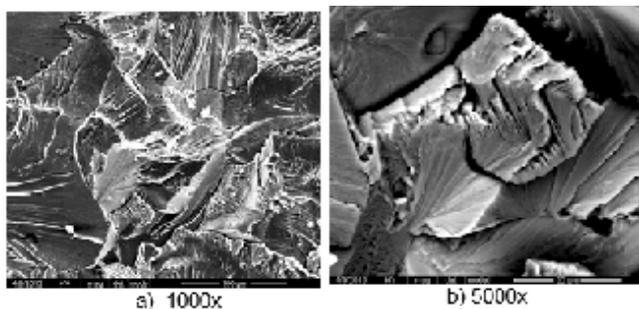


Fig. 6. SEM images of the AlCrFeCoNi alloy fracture surfaces

Table 2
CRYSTALLITE SIZES OF AlCrFeCoNi SAMPLES

	HEA1	HEA2	HEA3	HEA5	HEA6	HEA7	HEA8	HEA9	HEA10
Crystallite size [nm]	20.13	33.11	43.10	22.05	23.96	27.11	27.49	28.53	40.41

concentration of aluminum ($x = 2$, HEA 3) has been obtained the maximum diameter of crystallite of 43.10nm, that has also the maximum value of microhardness. The smallest values for crystallite size were obtained in samples HEA 1 (20.10 nm), HEA 5 (22.05 nm) and HEA 6 (23.96 nm).

Conclusions

The main element that influences the microhardness of the analyzed system is aluminum, due to the formation of hard Al-Fe compounds. Linear evolution of hardness depending on the concentration of alloying elements Cr, Fe, Co and Ni, confirm that they are contributing to lower of overall hardness of the alloy with high entropy AlCrFeCoNi by ensuring the conditions for forming solid solution.

From an overall perspective, X-ray diffraction and micro hardness analysis suggest that addition of the aluminum in AlCrFeCoNi alloy system contribute to forming of α -type solid solution. This type of solid solution increases the hardness of the alloy. The hardening of FCC phase can be attributed to the formation of some hard phases like AlFe and Al₂Fe, at 2Theta angle of 44.169°, respectively 81.332° and also by the appearance of AlCrFe₂ compound, having predominant peak detected at 2Theta angle of 64.355°.

The width and difference in chemical composition between the dendritic and interdendritic regions can be attributed to the non-equilibrium solidification mode, that favors this effect, known as interdendritic segregation. The microstructure is finer when the crystallization germs are more numerous and more evenly dispersed. On the interdendritic zone the high melting points elements are segregated, as form of crystallization germs, while the elements with low melting points remained in liquid zone, being pushed by the crystallization line.

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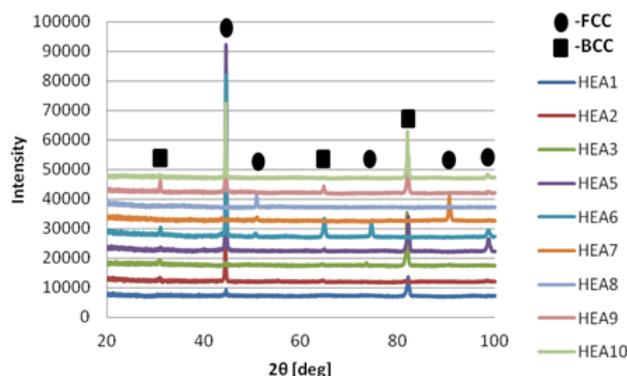


Fig. 7. XRD patterns of AlxCrFeCoNi alloys

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