Researches Regarding the Influence of Chemical Composition on the Properties of Al_xCrFeCoNi Alloys

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In this study Al_xCrFeCoNi (x, values of molar ratio, x = 1.0, 0.8 and 0.6) were prepared using a vacuum arc melting method. The aluminium addition on the microstructures, hardness and tenacity for these high entropy alloys were investigated. Al_xCrFeCoNi microstructures present well defined dendrites and interdendrite spaces with polyhedral compounds and precipitates in the vicinity of the grain boundary. The eutectics obtained are very fine and homogeneously dispersed within the matrix when x = 1.0 and segregations appear due to chromium grain refining effect and decrease of aluminium content (x = 0.8 and 0.6). As aluminium content decreases the hardness decreases dramatically, with 55% and the tenacity was improved with approximately 7.7%.

Keywords: high entropy alloy, chemical composition, microstructure, hardness, tenacity

High entropy alloys were developed during the last years as a class of materials consisting in, ideally, solid solution of five or more elements present in 5 – 35 at % [1-5]. Their microstructure is practically "frozen" at the melt level, embedding in solution a very different chemical elements conglomerate (elements as Cr, Ni, Co forming solid solutions with Al, a transitional metal with different solubility in Fe, Cr, Ni and Co) [6-9]. This joining creates entropy with high values and explains achieving different characteristics than simpler alloys. One or two solid solutions are formed, function of alloying elements percentage, embedding the other alloying elements. The dendrites microstructure is dominant and acicular or spheroid compounds can be observed depending on 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 (BCC or FCC) 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 (eg. Co and Ni forms a continuous solid solution (CoαNi) but can also dissolve in Fe stabilizing the austenite; for 17%Fe in Co, Fed can be found; solubility of Co in Cr is high (approx 12% Co) at ambient temperature or solubility of Co in Cr is appreciable) [10].

In [11] were studied the evolution and microstructure, hardness and corrosion properties of Al(0.5)CoCrFeNi alloy. This papers aims to study the evolution of microstructure and mechanical properties of Al_xCrFeCoNi, were x values are 0.6, 0.8 and 1.

Elemental composition is a critical factor in alloy design, which will definitely affect the alloying behaviour and properties of high entropy alloys. Many high entropy alloys systems have been reported recently, most of them containing aluminium [12]. The addition of aluminium has a considerable effect on the structure and properties of high entropy alloy due to its large atomic radius. For advanced consolidating effect elements forming hard compounds can be added (ex: eutectics Al_2Fe, Al_5Fe_2, $AlFe_3$) but do not determine the brittleness due to the fact that the compounds are embedded in a tough matrix with stable and strong interfaces.

The aluminium content can strengthen high – entropy alloy system achieving excellent mechanical properties. Hence, this paper present a series of high - entropy alloys, in the AlCrFeCoNi class, with different aluminium content, synthesized by vacuum arc remelting (VAR). The studies were conducted to investigate the microstructure and mechanical properties of Al_xCrFeCoNi.

Experimental part

All alloying elements with advanced purity were melted in a vacuum arc remelting installation (with current values till 500A), in controlled atmosphere (MRF ABJ 900).

We obtained 3 different compositions varying the quantity of aluminium considered with an important influence on the mechanical properties. The experimental charges were: HEA 1 – AlCrFeCoNi; HEA 2 – $Al_{0.8}$CrFeCoNi; HEA 3 – $Al_{0.6}$CrFeCoNi. The alloying elements were selected according to the chemical composition point of view and sizing analyses to be well placed in the cavities in the copper plate cooled with water. The losses during processing the high entropy alloys are low because the experiments were developed under argon or vacuum atmosphere. To ensure an increased homogeneity of the alloys, the charge was remelted for 5 to 7 times with successive turning of the experimental samples formed in every cavity.

The hardness was measured for each sample in five points with the aid of Shimadzu HMV 2TE tester and the mean values were calculated. The Charpy tests were realized on a Charpy pendulum measuring the absorbed energy value in the process of dynamic fracture by a standardized sample. The microstructure was realized by SEM microscopy. The composition analysis (EDS) of high-entropy alloys in solid samples, with detection range from ppm to 100%, has been done using X-ray fluorescence spectrometer by wavelength type S8 TIGER 1 KW – Bruker.

Results and discussions

Microstructure and chemical composition analysis

Figure 1 shows the SEM microstructures of Al_xCrFeCoNi were x is 1.0.

When x = 1.0 the phases are uniformly distributed. The dendrites have different orientations (fig. 1a) but at a closer

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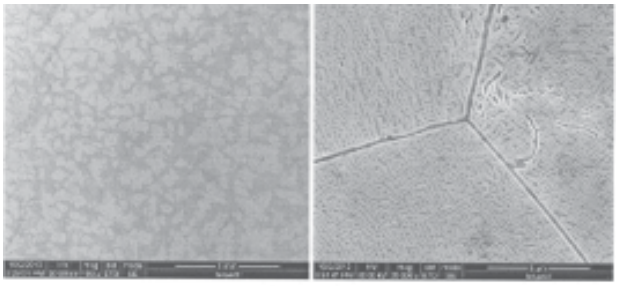

Fig. 1a. AlCrFeCoNi with dendrite with different orientation; b. AlCrFeCoNi microstructure at a higher magnification

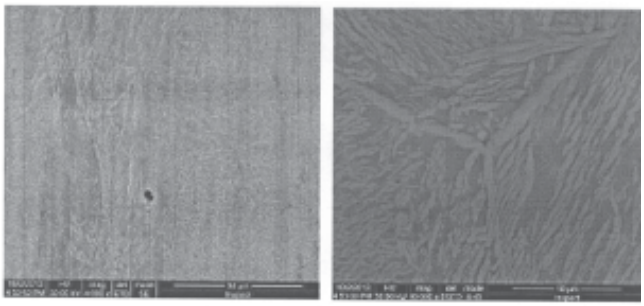

Fig. 2a. $Al_{0.8}$CrFeCoNi microstructure revealing the acicular and polyhedral compounds; b. $Al_{0.8}$CrFeCoNi microstructure at a higher magnification

look the eutectic formed (fig. 1b) have acicular shape and the grain boundaries are well defined. The grain size decreases to submicronic and nanometric range in this case and a susbtantial amount of enthalpy can be stored in nanocrystalline alloys due to the large grain boundary area.

The microstructure in figure 1b reveals a good homgeneity of the high entropy alloy obtained. Near the interface region are some compounds due to elemental segregation determined by aluminium addition. When x = 1.0 eutectics Al_2Fe, Al_5Fe_2, $AlFe_3$, usually BCC hard compounds, can be found in the microstructure and the hardness will be increased (table 2).

When aluminium content decreases, x = 0.8, the amount of FCC phase increase and the microstructure is modified (fig. 2a and b). FCC phase has less crystallographic slip planes and determine a less desirable property for high entropy alloy, as increased ductile to brittle temperature. The typical dendrites appear and acicular and polyhedral compounds can be seen in interdendrite region. The dendrite region is rich of Co and Ni (lighter regions) (as is observed in the EDX in table 1) and interdentrite region is rich of Fe and Cr (grey regions). The elemental segregation can be explained by mixing enthalpies among principal metallic elements [12]. From mixing enthalpy of binary equiatomic alloys Cr and Fe have relatively higher mixing enthalpies with other elements. Thus Cr and Fe are repelled from dendrites regions enriching the interdendrite region in Cr and Fe.

In figure 2b the same eutectic structure as for AlCrFeCoNi can be observed in interdentrite region. The dendrites in case are elongated in comparison with figure 1a were the dendrites are like flaxes.

When the aluminium content was lowered, x = 0.6 (fig. 3a and b) the dendrites compounds, needle compounds and fine interdentrites precipitates appeared in the microstructures. The dendrites are larger and the influence of small aluminium content is emphasized. The dendrites seem to be rich in Co and Ni as in previous two high entropy alloys studied. In interdendrite region the Fe and Cr phases are seen (grey regions). These regions enriched in αFe and Cr has been also reported [13].

The chemical compositions of the Al_xCrFeCoNi high entropy alloys nominal and determined with EDS analyses, inside the dendrite and interdendrite regions are shown in table 1.

Mechanical properties

The $HV_{0.1}$ hardness was measured for each sample in 10 points and the mean value was calculated. The mean values are shown in table 2.

AlCrFeCoNi high entropy alloys hardness decrease proportionally with the aluminium content, decreasing from 500$HV_{0.1}$ for HEA 1 (AlCrFeCoNi) to 407 $HV_{0.1}$ for HEA 2 ($Al_{0.8}$CrFeCoNi) and respectively 224 $HV_{0.1}$ for HEA 3 ($Al_{0.6}$CrFeCoNi). The hardness decreasing could be explained by reducing quantity and the number of hard precipitate (Fe-Al compounds) in metallic matrix and increasing the amount of FCC phase. Alloys from AlCrFeCoNi class have a high compression resistance, yield resistance and tension, measured values being 2004 MPa, 1250 MPa and respectively 32.7 % [11, 14]. The chromium is repelled in interdendrite spaces due to higher mixing with other elements enthalpies and has a grain refining effect determining the changes in high – entropy alloys plasticity. The hardness values are homogenous within the

Alloy	Zone	Al	Cr	Fe	Co	Ni
AlCrFeCoNi	Nominal (wt%)	10.67	20.55	22.13	23.32	23.33
	Dendrite (wt%)	13.04	20.13	22.19	22.43	22.22
	Interdendrite (wt%)	12.79	20.86	22.26	22.33	21.77
$Al_{0.8}$CrFeCoNi	Nominal (wt%)	8.72	21	22.61	23.82	23.85
	Dendrite (wt%)	9.31	24.18	22.25	22.54	21.72
	Interdendrite (wt%)	7.98	26.63	23.32	22.15	19.92
$Al_{0.6}$CrFeCoNi	Nominal (wt%)	6.68	21.47	23.12	24.36	24.36
	Dendrite (wt%)	8.57	22.28	22.99	22.55	23.61
	Interdendrite (wt%)	5.74	20.89	26.10	24.88	22.38

Table 1
CHEMICAL COMPOSITION OF Al_xCrFeCoNi (x = 1.0, 0.8 AND 0.6) IN wt%, DETERMINED BY EDS ANALYSES

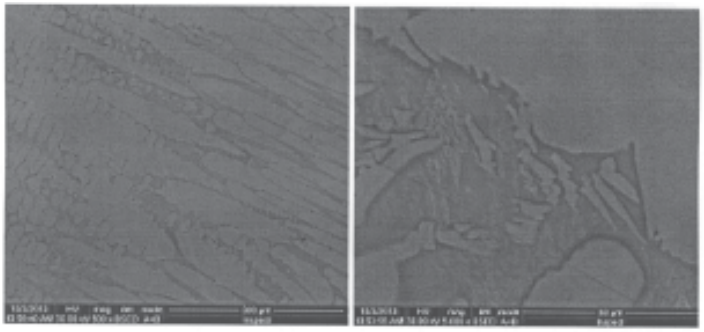

Fig. 3a. $Al_{0.6}CrFeCoNi$ microstructure revealing large dendrites; b. $Al_{0.6}CrFeCoNi$ microstrure at higher magnification revealing polyhedral compounds and fine preciitates

Alloy	AlCrFeCoNi	$Al_{0.8}CrFeCoNi$	$Al_{0.6}CrFeCoNi$
$HV_{0.1}$	505.8	407	224

Table 2
THE $HV_{0.1}$ HARDNESS FOR $Al_xCrFeCoNi$ (x = 1.0, 0.8 and 0.6)

Alloy	AlCrFeCoNi	$Al_{0.8}CrFeCoNi$	$Al_{0.6}CrFeCoNi$
Mean value	62.27	67.15	67.47

Table 3
ABSORBED ENERGY DURING CHARPY TEST FOR $Al_xCrFeCoNi$ (x = 1.0, 0.8 AND 0.6)

direction of the samples proofing also a good homogeneity of the sample and is twice comparing with carbon steel. For hardening the solution, the incorporation of the strongest binding element Al and the high melting point element Cr into BCC lattice increase the Young modulus and slip resistance. The atomic size difference (Al having the atomic radius 1.43Å and Cr 1.24Å, like Fe, Co and Ni having the atomic radius 1.24Å, 1.25 Å and respectively 1.25Å) is also a factor influencing solution hardening. Al, the largest atom will increase the lattice distortion and resist the slip [15]. When the Al amount decreases the effect decreases and the hardness value decrease as well.

Usually if a material hardness value is elevated, then the material presents a high plasticity and low tenacity. The investigations upon the high entropy alloy tenacity behaviour were realized by Charpy test. The Charpy tests were realized on a Charpy pendulum measuring the absorbed energy value in the process of dynamic fracture by a standardized sample. Five samples were tested, for each composition and the mean value was calculated and shown in table 3.

The fracture energy is in the 62…67J interval with hardness oscillating between 200 – 500 $HV_{0.1}$. As a direct consequence the hardening effect will not decrease the metallic matrix tenacity in the case of analyzed high entropy alloys.

Conclusions

$Al_xCrFeCoNi$ high entropy alloys as-cast were successfully obtained and characterized. The decrease of aluminium content proved to have strong influence on high entropy alloys hardness. The alloys hardness decreased with 55% as the aluminium content decreased from x = 1 to x = 0.6. Although the high entropy alloy tenacity increased slightly, with 7.7% with aluminium content decreasing.

The dendrite region of high entropy alloys obtained is proved to be rich in Co and Ni and the interdendrite spaces are rich in Cr and Fe. When there are the hard compounds as Al_2Fe, Al_5Fe_2, $AlFe_3$ (when x = 1.0) the hardness value is 505.8, twice as a carbon steel. The fracture energy is in the 62…67J interval with hardness oscillating between 200 – 500 $HV_{0.1}$. As a direct consequence the hardening effect will not decrease the metallic matrix tenacity in the case of analyzed high entropy alloys.

Acknowledgment: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number PCCA No. 209/2012 – "Composite Structures Resistant at Dynamic Loadings Applied with High Deformation Speeds Used in the Field of Collective Protection - HEAMIL".

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Manuscript received: 16.12.2013