Influence of the Chemical Composition on the Microstructure and Microhardness of AlCrFeCoNi High Entropy Alloy

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The high entropy alloys (HEA) have much higher entropy of mixing, at atomic scale, than traditional alloys in liquid state or random solid solution state. Recent developments in the field of high-entropy alloys have revealed that they have versatile properties like: ductility, toughness, hardness and corrosion resistance. In the paper are presented some results regarding the effect of chemical composition variation (Nickel content increasing) on the microstructure and microhardness of high entropy alloys from AlCrFeCoNi system. It was found that by increasing the Nickel content the microhardness values have decreased, but have been achieved high values of plasticity and the homogeneity of the solid solution has been improved. By applying heat treatments, it can be obtained different pairs of hardness and plasticity, depending on the dedicated application.

Keywords: high entropy alloy, chemical composition, Nickel, microstructure, microhardness

Complex homogeneous materials or composite materials are mainly used to ensure a good resistance and toughness to projectile penetration and high energy absorption, characteristics that are considered mandatory for manufacturing of devices used for individual and/or collective protection. It has been shown that certain light metal alloys (aluminum, magnesium or titanium alloys) and certain polymers are capable to provide a good level of impact resistance [1, 2].

The main features that the material must have, in order to ensure the best possible impact behavior, are as follows [3]:

- high values of hardness, as a measure of resistance to penetration of solid material by different types of projectile, with permanent changes in shape when a force is applied on them by static or dynamic mode. Macroscopic hardness is generally characterized by the nature and strength of the intermolecular bonds;
- high-Toughness, expressing the capability of absorption of energy for breaking and crack initiation or resistance to crack propagation, considering the high velocity of energy absorption during impact plastic deformation;
- impact resistance that is relative susceptibility to material breaking by the action of forces applied with high speed.

Generally, the entropy is defined as a thermodynamic function that characterizes the energy involved in arranging and rearranging of the elementary particles of matter (molecules, atoms, ions, electrons). All spontaneous processes are accompanied by an increase in entropy of the system, and the entropy of any system (including the Universe) tends to a maximum value [4, 5].

High entropy alloys are composed of “n” major alloying elements with $n \geq 5$, introduced into molar or nearly equivalent rates that lead to the formation of solid solution phases, with simple network type (f.c.c. or b.c.c.), nano-structures and even amorphous state [6]. Therefore, the high entropy alloys are solid solutions with high strength, good thermal stability, and greater quenching capacity than conventional alloys, combined with superior resistance to various environmental conditions [7].

In recent studies from scientific literature on certain types of high entropy alloys have been analyzed the effects of adding (or varying) certain chemical elements (such as Al, B, Ni, Cr, Ti, Fe and V) on the microstructure and mechanical properties. Alloying elements having different values of network parameters can affect as well both crystalline microstructure and properties of these alloys. So far, have not been fully clarified all these effects, and especially is not know exactly if there is a correlation between the electronic configuration of alloying elements and general microstructure [6, 8]. In the paper was studied the effect of chemical composition (by increasing the Nickel content) on the properties of high entropy alloys from AlCrFeCoNi system.

Experimental part

The high entropy alloys from AlCrFeCoNi system were obtained at ERAMET laboratory of Politehnica University of Bucharest using a vacuum arc remelting equipment (VAR), model MRF ABJ 900 VAR. The device has the following technical characteristics: melting power – min 55kVA; melting current – min 650 A@ 60%DS, tri-phase voltage; maximum temperature – 3700°C; maximum level for vacuum obtained by preliminary vacuum and diffusion pumps: 10^{-6}mbar; inert gas feeding system – argon; furnace chamber – stainless steel, double walls water cooled; copper base plate, water cooled having the following dimensions: Φ 230 mm x 13 mm (thickness); non – feeding electrode made from tungsten with Φ 65, mm.

For obtainment of high entropy alloys it was used a clean charge (raw materials), with high preparation quality and low content of P and S, having in view that the VAR technology cannot allow the development of dephosphorization and desulphurization processes. The charge is composed by materials with high purity: ARMCO Iron, metallic Cr, electrolytic Ni, metallic Co and Al.

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Fig. 1. High entropy alloy (HEA) reference sample.

Table 1
CHEMICAL COMPOSITION OF
THE HIGH ENTROPY ALLOYS, %

Alloy type	Al	Cr	Fe	Co	Ni
HEA 1 - Ni 1	10.67	20.55	22.13	23.32	23.33
HEA 11 –Ni 1.2	10.2	19.64	21.15	22.48	26.74
HEA 12 – Ni 1.4	9.76	18.8	20.24	21.33	29.86
HEA 13 – Ni 1.6	9.36	18.03	1.42	20.45	32.73
HEA 14 – Ni 1.8	8.99	17.32	18.65	19.65	35.38
HEA 15 – Ni 2	8.65	16.66	17.95	18.91	37.82

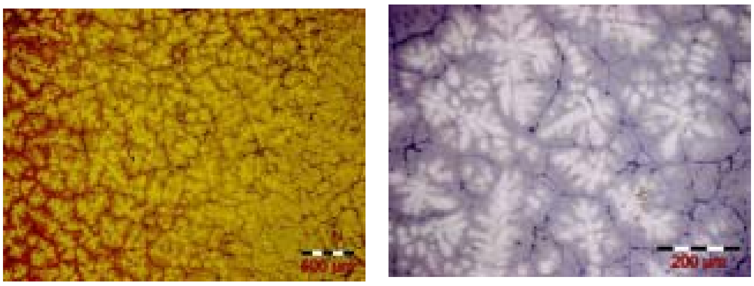

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Fig.2. Optical microscopy images of HEA1 (AlCrFeCoNi). Dendritic formations and fine precipitates localized on grain boundaries and in grain volume: a) Magnification 50x; b) Magnification 200x.

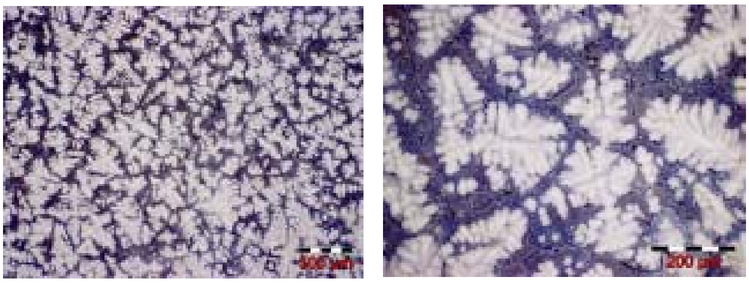

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Fig.3. Microstructure of HEA 11:
a) Magnification 50x;
b) Magnification 200x.

For the charge calculus the theoretical chemical elements assimilation degree into the melt was considered and also the eventual losses by vaporizing during the vacuum process developing. By calculation of the percentage participation of each element, the recipes for hyper-entropic base alloys were established. It contains molar equivalent percents of Al, Cr, Co, Ni, and Fe. The working conditions have been similar for all samples, meaning reaching a minimum pressure of 10^{-4} mbar inside the working chamber, followed by filling with 99.999% Ar, providing the oxygen content inside the working chamber with a value of 60 ppm. Melting was realized with the aid of electric arch between the tungsten electrode and metallic charge in the water cooled base copper plate. The melting power was minimum 55 kVA and the melting current was minimum 650A@60%DS tri-phase voltage.

In order to obtain an adequate homogeneity, the alloy was re-melted in VAR unit for 3 times on both surfaces, using inert atmosphere of Argon [9]. There were obtained several test samples in the form of rods (fig. 1).

Results and discussions

To study the effect of Nickel content increasing on the hardness values and microstructure of high entropy alloys, were obtained 6 types of alloys, in which was gradually increased the content of Ni between 1 and 2 % at. (table 1).

Microstructural Analysis

Samples were prepared, for metallographic analysis by optical and electron microscopy (SEM), in accordance with the metallographic sample preparation procedure of LAMET laboratory from Politehnica University of Bucharest [10]. By using optical microscopy examination at different magnifications has revealed the dendritic morphology of high entropy alloy, in as-cast form, for the reference alloy AlCrFeCoNi (HEA1) (fig. 2).

The quenching of Ni-rich alloys (65 at % Ni) from high temperatures (1200°C) leads to formation of martensitic microstructures tetragonal centered and twisted [11]. The increasing of Ni content also causes microscopic changes, by increasing the width of interdendritic zones (fig. 3).

By increasing the Nickel content, some microstructural changes occur, meaning that the dispersed solid solutions are changing with continuous solid solutions. Since the solubility of aluminum in Nickel is about 20 % at 1385°C, the increasing of Nickel content conducted to increasing of the solubility domain for aluminum.

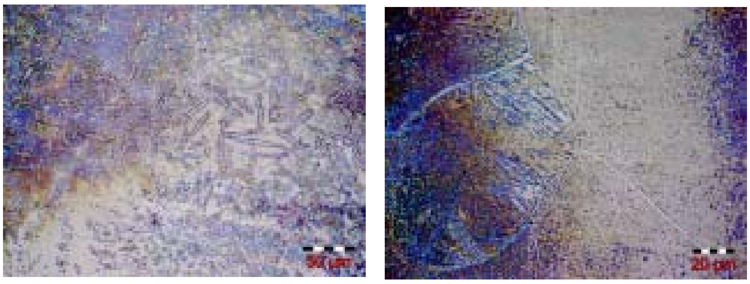

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Fig..4. Microstructure of HEA 12:
a) Magnification 50x;
b) Magnification 200x.

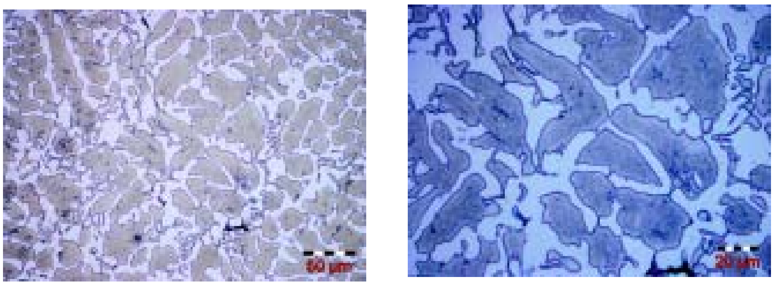

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Fig. 5. Microstructure of HEA 13:
a) Magnification 50x;
b) Magnification 200x.

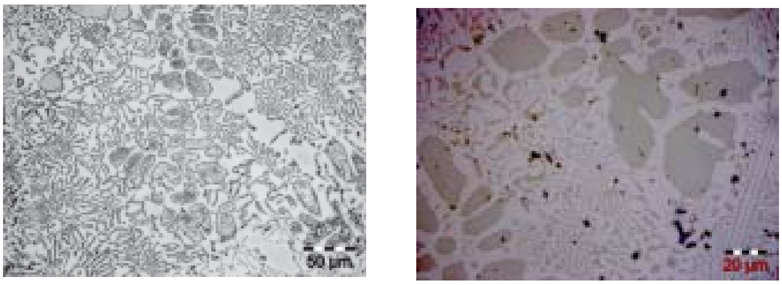

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Fig. 6. Microstructure of HEA 14:
a) Magnification 50x;
b) Magnification 200x.

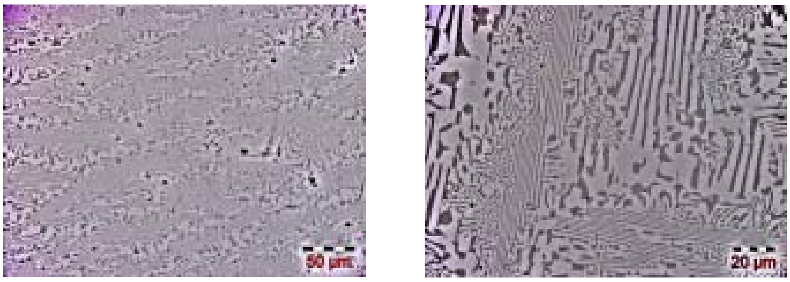

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Fig. 7. Microstructure of HEA 15:
a) Magnification 50x;
b) Magnification 200x.

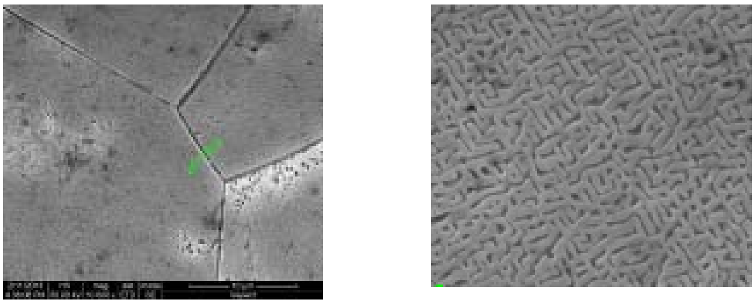

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Fig. 8. High entropy alloy microstructure at high magnification, showing fine lamella and rod eutectic (specimen etched electrochemically in oxalic acid 10%). SEM microscopy (x10000).

Elements such as Fe, Co, Ni and Al can form continuous solid solutions, the equal content being both in interdendritic zones and in dendrites, while Cr are segregated in interdendritic regions, more than in dendrites.

For the maximum analyzed level of Nickel (2% at. Ni, fig. 7), during examination with higher magnification, has been revealed a tendency of arrangement of eutectic formations, in ordered geometry, similar to magnetic fields in amorphous alloys.

At high magnification (10000 X) the microstructure of high entropy alloy has a very fine dendritic network, with clear delineation of grain boundaries, having the width of about 240µm (fig. 8).

Microhardness Tests

The microhardness was measured in cross section for the 6 types of high entropy alloys, using a Shimadzu HMV 2T device. The test load was 9.807 N and the test duration was 10 s; ten indentations were performed for each sample and the average values are presented in table 2.

Alloy type	HEA1	HEA11	HEA12	HEA13	HEA14	HEA15
Hardness average value	543	502	478	330	324	298

Table 2
MICROHARDNESS VALUES, HV1/10

Conclusions

It can be concluded that by increasing the Ni content of high entropy alloys lead to a microstructure consisting of dendritic formations, eutectic zones and large interdendritic spaces.

The hardening effect in mixed alloys Al-Cr-Fe-Co-Ni, appears due to the super saturation effect in solid solutions, that depends on chemical composition. Hardness values decrease with increasing the percentage of Nickel, as effect of dissolution of precipitates in a Nickel rich matrix, to form continuous solid solutions.

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