Investigations on composites reinforced with HEA particles

I Carcea¹, R Chelariu², L Asavei¹, N Cimpoşu⁴ and R M Florea⁵
¹,²,³,⁴,⁵Department of Materials Science and Engineering, “Gheorghe Asachi”
Technical University of Iasi-Romania, 59A Mangeron Blvd., 700050, Iasi, Romania
E-mail: raluca.m_florea@yahoo.com

Abstract. This work reports the results of investigations on the fortification with high entropy alloys particles of aluminium matrix composite materials. The properties of these materials processed by Vortex techniques primarily depend on the matrix and the volume fraction of the constituent phase. The mechanical properties, toughening mechanisms and potential applications are briefly reviewed. Traditional methods were used for the basic characterization of the composite. The microstructure of the composites were investigated by optical and scanning electron microscopy (OM, SEM). SEM analysis was performed in order to observe the microstructural evolution as a function of the HEA particles content and to identify some reasons of the presence of porosity or any irregularities within the metal matrix.

1. Introduction
The tests for obtaining new materials with high performance have led to the development of a class of products known as composite materials. By definition, the concept of composite is assigned to a complex system, composed of different materials with different nature. In this category are falling under a various a class of materials. This is caused by the fact that the possibilities for amending of the basic manufacturing techniques, the level of performance and cost are manifold [1, 2].

Metal matrix composites have been developed primarily from the need to increase its physical-mechanical performance and weight reduction of machines and machinery, as well as to the continuation of their work duration. Through the introduction of reinforced materials it could replace heavy ferrous alloys with the light non-ferrous metals (Al, Mg) due to betterment of antifriction properties, strength, elasticity module, resistance to wear etc. As a complementary material are used metal fibers, non-metallic fibers or particles with varied of chemical nature, size and shape [3, 4].

For large-scale applications, including the sectors of transportation, entertainment and sport are needed materials that can be obtained with not too big expenses like Al alloys reinforced with particles of silicon carbide, alumina, etc. Particle reinforced composite materials have evolved in recent decades because they are cheaper and have higher-valued properties than the classic materials, which can be enumerate as: great elasticity, good mechanical resistance, high ductility, high resistance to the propagation of cracks etc. Thus, the addition of particles in an aluminum alloy can inhibit the propagation of cracks and increases the resistance to tearing of the alloy [5, 6]. In this paper are used high entropy alloy particles, FeNiCrMnAl, for the reinforcement of an aluminum alloy matrix.

The reinforcement of the alloy matrix with HEA particles gives to the low density composite materials a multitude of attractive features, such as high hardness, very good resistance to wear,
fatigue resistance, a very good tensile strength at elevated temperatures, thermal stability and resistance to oxidation and corrosion.

Alloys with high entropy (HEA) represent a new class of metallic materials with a distinct strategy of synthesis. They are different from conventional alloys which are based on one or two main elements because they are composed of five or more items.

2. Thermodynamic aspects of HEA
Alloys with high entropy have been granted special attention in recent years, developing more than 300 kinds of alloys in this category. Most scientific studies of the literature focused on investigating the correlation between microstructure, phase composition and mechanical properties.

Development of multicomponent alloys needs a deeper understanding of the thermodynamic aspects that define these alloys [6-9].

The Entropy is a thermodynamic unit which can be used to determine the energy available for useful work in a thermodynamic process.

The thermodynamic Entropy represents the ratio between the amount of heat available in a system and the temperature of the system, being defined by the following equation:

$$dS = \frac{\Delta Q}{T}$$  \hspace{1cm} (1)

where $S$ is the entropy, $Q$ is the quantity of heat, and $T$ is the absolute temperature.

For estimating the formation entropy of a metallic alloy, Boltzmann hypothesis asserts that this has the maximum value in the case of equiatomic compositions, as a result of the following formula:

$$\Delta S = -k \ln w = -R\left(\frac{1}{n \ln 1/n} + \frac{1}{n \ln 1/n} + \ldots + \frac{1}{n \ln 1/n}\right) = -R \ln \frac{1}{n} = R \ln n$$  \hspace{1cm} (2)

where $R$ is the ideal gas constant and $n$ is the number of elements in the system. Starting with $n = 5$, $\Delta S$ becomes higher than the majority of intermetallic compounds leading to preferential formation of solid solutions. In the interval $5 \leq n \leq 13$, the alloys have entropies with values between $1.61 \, R$ and $2.56 \, R$ and belong to the domain of high entropy.

For the alloy systems, mixing Gibbs free energy, can be expressed as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$  \hspace{1cm} (3)

where $\Delta G_{\text{mix}}$ is the Gibbs free energy, $\Delta H_{\text{mix}}$ is the mixing enthalpy, $\Delta S_{\text{mix}}$ is the mixing entropy and $T$ represents the absolute temperature.

In the obtaining high-entropy alloy the greatest challenge is the prediction of phase stability (e.g. number of equilibrium stages and molar ratios), depending on the temperature and chemical composition. According to the Hume-Rothery rule the difference between the Atomic sizes ($\delta$) and enthalpy of mixing ($\Delta H_{\text{mix}}$) are two determining factors. In the case of HEA alloys, the two parameters are defined as follows:

$$\delta = \sqrt{\sum_{i=1}^{N} c_i \left(1 - \frac{r_i}{\sum_{i=1}^{N} c_i r_i}\right)}$$  \hspace{1cm} (4)

$$\Delta H_{\text{mix}} = \sum_{i=1}^{N} \sum_{i \neq j} 4 \Delta H_{AB}^{\text{mix}} c_i c_j$$  \hspace{1cm} (5)

where $r_i$ is the Atomic radius of the component $i$ and $\Delta H_{AB}^{\text{mix}}$ is the mixing enthalpy for binary items A and B.
3. Materials and methods
For the obtaining of an experimental metal-metal composite were used an aluminum alloy: ATSi6Cu4 in accordance with SREN 1706 – 2000, and high entropy alloy particles with following composition: Fe29Cr28Mn19Ni18Al5Si.

The matrix alloy was melted and overheated in a silicon carbide crucible in a furnace with electric resistors. The melting point of the matrix alloy is about 650°C, and the overheating point was up to 730°C. HEA particles were obtained from a half-broken cast and then milled into a conventional mill.

To obtain experimental composites it was used the Vortex method. The preheated HEA were added in a cyclone cone, formed by blades which were mixing the liquid matrix alloy and the particles together. Observing the technological flow shown in figure 1 were developed three types of composite materials with different proportions of reinforcement: Al/HEA10, Al/HEA15 and Al/HEA20. For investigation of structure and uniformity was chosen the composite material with 20% reinforcing particles, obtained under the conditions outlined.

![Technological flow for obtaining of Al/HEA\_\_\_ composites.](image)

Figure 1. Technological flow for obtaining of Al/HEA\_\_\_ composites.

4. Experimental studies
4.1. Al/HEA\_\_\_ composite microstructure
Microstructural analysis of Al/HEA20 composite was performed by electron microscopy on a SEM Vega Tescan LMH.

Particles distribution and composite morphology have a significant influence on the mechanical and tribological properties. Therefore, the main task during the production of composite materials with aluminum matrix is to achieve evenly distributed particle reinforcement [6, 11-13].

Even though the contact angle formed at the interface is much less than 90° and the matrix alloy wets the reinforcement particles, in cast and solidified samples was observed some HEA particle segregations. This settling of particles reinforcement to the lower side of samples is due to the difference between the density of the HEA, which is approx. 7.2 kg/dm\(^3\), in relation to that of liquid aluminum alloy, which is 2.5 kg/dm\(^3\).

Figure 2a shows a SEM microscopy of the composite. It is easily observed that the particles were uniformly embedded in the Al alloy matrix. Figure 2b illustrates the distribution of the elements that are forming both the matrix and the particles. Also this image attests the uniform distribution of HEA particles.

In figure 3 it is observed that HEA particles are embedded in the Al alloys matrix. The HEA were measured and their size is greater than 560μm.

Figure 4 shows a qualitative analysis of of the Al/HEA20 composite. It is noted the presence of chemical elements from the composition of both: the HEA particles and the Al alloys matrix. It can be easily made distinguish between the matrix and the reinforcement by distribution of elements as:
chemical elements like Mn, Fe, Cr, Ni are found only in some parts of the image which shows that the particles are incorporated evenly and not gathered in the form of gatherings. The matrix elements, as Al, are present with no discontinuity what means that in the composite structure was not formed cracks or defects.

![SEM microscopy](image1)
![EDS microscopy](image2)

**Figure 2.** SEM micrographs of Al/HEA<sub>20</sub> composite.

![Micrographs with details](image3)

**Figure 3.** Al/HEA<sub>20</sub> micrographs with details on embedded HEA particles.

![Qualitative analysis](image4)

**Figure 4.** The qualitative analysis (EDX) which shows the chemical composition of Al/HEA<sub>20</sub> composite.
Figure 5 is focused on chemical elements that are constituting the obtained composite. Was noticed that the predominant element in the matrix is Al. The content of Al decrease, but remain present, in the areas where are embedded particles of HEA, and concentration of elements such as Fe, Ni, Cr, Mn increases. This fact reinforces the claim that particles are embedded in the matrix without forming cracks in composite structure.

![Figure 5. SEM microscopy and distribution of chemical elements of Al/HEA_{20} composite.](image)

4.2. Experimental results of Al/HEA_{\theta} composite coefficient of friction

For monitoring the friction coefficient was used a Universal-2 UMT tribometer, which has a sensor that measures the real-time force of rubbing and friction coefficient calculated on the basis of the normal force and the force resistant test at some time t [10].

The force of friction coefficient is given by:

\[ \mu = \frac{F_f}{F_n} \]  

(6)

Tribological parameters for analyzing the three types of composites Al/HEA_{10}, Al/HEA_{15} and Al/HEA_{20} have following values: t = 1800 sec, F_{x} = 10 N.

The time course of the coefficient of friction for the three obtained composites was shown in figure 6.

![Figure 6. Friction coefficient for the three types of obtained composites.](image)

The analysis of the friction coefficient of composite with 10% HEA_{\theta} has proved that in the first 25 seconds of tribological analysis were showed no fluctuations in frictional coefficient. In the range 25-597 sec held an increase of the friction coefficient \( \mu = 0.207 \); after this period, until 1800 sec, friction coefficient recorded a constant variation.
In the case of composite with 15% HEA_p was noted that during the first 397 seconds, friction coefficient recorded an increase. In the intervening period 397-1800 sec appeared small fluctuation of the coefficient of friction. The value of the coefficient of friction for the composite with 15% HEA_p is equal to $\mu = 0.202$.

Analysis on the tribological behavior of composite with 20% HEA_p gave the value of coefficient of friction equal to 0.173.

For a comparison of the three analyzed composites the value of coefficient of friction has a slight decrease due to the increase in the percentage of HEA particles from composite material. This was explained by the fact that HEA particles have a very good resistance to wear.

The highest value of the coefficient of friction in the first 400 seconds was for the composite with 10% HEA_p, having the value of $\mu = 0.200$.

5. Conclusions

By Vortex method has been successfully developed three types of metal-matrix composites reinforced with metal particles.

Images taken using electronic microscope SEM and qualitative analyses EDX of Al/HEA_{20} composite proofs that particles were uniformly distributed throughout the matrix without causing cracks in the composite.

Obtained composite values for friction coefficient are very good, increasing it by addition of HEA_p.

6. References

[1] Florea RM, Peter I, Rosso M, Mitrică D and Carcea I 2013 JOAM 7-8 833
[2] Bălțătescu O, Florea R M, Roman C, Rusu I and Carcea I 2013 JOAM 7-8 823
[3] Elsayed A, Kondoh K, Imai H and Umeda J 2010 Mater. Des. 31 2444
[4] Rusu O 2017 Superlight composite materials with metallic matrix (Iasi-Romania, PIM)
[5] Wang ZW, Yuan Y, Zheng RX, Ameyama K and MA C 2014 Trans. Nonferrous Met. Soc. China 24 2366-2373
[6] Singh J and Chauhan A 2016, Ceram. Inter. 42 (1A) 56-81
[7] Selvakumara S, Dinaharane I, Palanivele R and Ganesh B 2017 Mater. Sci. & Eng. A 685 317-326
[8] Bedolla E, Lemus-Ruiz J and Contreras A 2012 Mater. Des. 38-91
[9] Miracle DB, Senkov ON 2017 Acta Materialia 122 448-511
[10] CETR UMT-2 Multi-Specimen Test System, Viewer Manual, Version 2.14 Build 77, 2007
[11] Nedelcu D, Comaneci R, Chelariu R, Tabacaru L, 2009 Overview of composite material technology with Si-C particles reinforcement International Journal of Modern Manufacturing Technologies, I (1), 57-63
[12] Nedelcu D, Carcea I, Tabacaru L, Ciofu C, 2011 Some aspects of processing and properties of composite material with Si-C particles, Acta Physica Polonica A, 120 (2), 344-348
[13] Carcea I, Nedelcu D, 2012 Technology for obtaining composite material with metallic matrix and Si-C particles, Materials and Manufacturing Processes, 27(6), 694-701