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Mechanically Alloyed High Entropy Composite

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Abstract: In the last years high entropy alloys have been investigated due to their high hardness, high temperature stability and unusual properties that make these alloys to have significant interest. In comparison with traditional alloys that are based on two or three major elements, this new generation alloys consists at least of 5 principal elements, with the concentration between 5 and 35 at.%. The present paper reports synthesis of high entropy alloys (HEA) and high entropy composites (HEC) synthesized by mechanical alloying (MA). The equiatomic AlCrFeNiMn matrix was used for creating the HEA matrix, starting from elemental powders and as reinforcing material for composites was used pure graphite. The mechanical alloying process was carried out at different duration, in a high energy planetary ball mill, under argon atmosphere. The elemental powders alloying began after 15 hours of milling and was complete after 40 hours. The mechanical alloyed matrix and composite was pressed and heat treated under argon protection. The elemental powers were investigated for physical - technological properties, and by X-ray diffraction and scanning electron microscopy. Phase pressing operation was realized with a hydraulic press and the applied pressure was progressive. The sintering process was carried out at 850°C for 2 h. The X-ray diffraction revealed that the MA process resulted in solid solutions formation and also revealed body-centred cubic (BCC) and face–centred cubic (FCC) structures with average grain size around 40 nm. In addition, nanoscale particles were highlighted by scanning electron microscopy, as well as the homogeneity of the chemical composition of the matrix and composite that was confirmed by EDX microanalysis. It was noted that HEA matrix and HEA composites were processed with a high degree of compaction and with a quite large capacity of mixed powder densification (around 70%).

Key words: high entropy alloy, composite, mechanical alloying, microstructure, properties.

1. Introduction

In general, most conventional alloys are composed of one principal element that represents at least 50 at% in the composition and in which are added minor alloying elements to improve microstructure and properties. High entropy alloys (HEAs) proposed by Yeh et al in 2004 [1] are defined as alloys with at least 5 principal elements, with concentration of each element from 5 to 35 at%. HEAs have

significantly higher mixing entropy than those of conventional alloys and should form mainly disordered solid solution structures, instead of intermetallic compounds [1,2,3,4,5]. Furthermore, because of the unique multi-principal element composition HEAs have special properties. These include high hardness, high strength, outstanding wear resistance, exceptional high temperature strength, good structural stability, good corrosion and oxidation resistance making them very interesting for engineering applications.

Among the different processing methods available for HEA synthesis, the most widely studied is by far the vacuum arc melting and vacuum induction melting followed by casting [6,7]. Another method to obtain HEAs is mechanical alloying followed by spark plasma sintering. By spark plasma sintering powders can be consolidated rapidly to a higher density by simultaneous pressing and sintering [8-11]. Only few researches reported their result for processing of HEAs by mechanical alloying followed by consolidation and sintering in argon atmosphere [12,13].

HEAs as composite material have not been investigated yet. For example, in one article is indicated the addition of carbon [14], but not as a reinforcing material.

Most investigated HEAs are: CoCrFeNiMn, NiCoCrCuFe, $FeNiCrCo_{0.3}Al_{0.7}$, $CoFeNiAl_{0.5}Ti_{0.5}$, AlCoCrCuFe, $Al_xCoCrCuFeNi$, $Al_{0.75}FeNiCrCo$, AlCrFeCoNiCu, $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$, etc.

$Al_xCrFe_{1.5}MnNi_{0.5}$ (x=0.3 or 0.5) high entropy alloy was investigated only in as-cast state, and was obtained by arc and induction melting [15,16]. The main purpose in studying this alloy system was to obtain less expensive HEA (the substitution of Co with less expensive Mn) with high strength and significant resistance to annealing softening. Also, they highlighted the dual-phase structure of BCC phase and FCC phase, in which Al, Ni-rich precipitates of B2 phase, or Cr-rich particles are dispersed.

Given the above discussion, the paper presents the results on synthesis and characterization of a high entropy alloy (AlCrFeMnNi considered as matrix) and a new high entropy composite (AlCrFeMnNi/Gr) by mechanical alloying (MA), followed by conventional powder metallurgy techniques.

2. Experimental

Equi-atomic pure elemental powders (higher than 99.5%) and particle size of ≤45μm were mechanically alloyed to synthesize AlCrFeMnNi matrix. Subsequently, same pure elemetal powders and graphite powder were used to synthesize AlCrFeMnNi/Gr composite. RETSCH PM 400 high energy ball mill was used for mechanical alloying of these powders. High performance stainless steel vials and balls were utilized as the milling media, ball to powder weight ratio being 10:1 and n-heptane was used as the process controlling agent. N-heptane was added as a process control agent to avoid excessive agglomeration of particles.The milling was carried out up to 40 hours, from 5 to 40 h, at 300 rpm. The mechanical alloying process was carried out at different duration, under argon atmosphere in order to prevent powders oxidation (Table 1). It was noticed that elemental powders alloying began after 15 hours of milling and was complete after 40 hours, so that only these data will be considered further.

Table 1. Samples grade in function of milling time.

Sample	AlCrFeMnNi	AlCrFeMnNi/Gr			
Marked Sample	HEA	HEC1	HEC2	HEC3	HEC4
Milling time, (h)	15	15	20	25	40

The elemental powers were investigated for physical - technological properties, by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Mechanically alloyed powders were consolidated with a hydraulic press. The applied pressure being increased progressive from 4 to 10 tf/cm^2 and the tests revealed that the appropriate pressure for the investigated samples was 10 tf/cm^2. The sintering process was carried out in a NEBARTHERM furnace with argon atmosphere at a temperature of 850°C for 2 h. The heating rate was 15^{0}C/min and the cooling rate was 10^{0}C/min.

The XRD carharacterization were carried out in X′Pert Pro Panalytical instrument. The microstructures of the milled and sintered powders were investigated using QUANTA INSPECT scanning electron microscope equipped with a field emission electron gun, and with energy dispersive analysis radiation X to determine the elemental distribution at different points across the sample.

3. Results and discussion

AlCrFeMnNi matrix (noted HEA) and AlCrFeMnNi/Gr (noted HEC) composite were characterized in terms of physical-chemical, technological and structural properties. The thermo physical-chemical properties of the elements chosen for HEA matrix and for graphite, that was chose as reinforcement for the HEA matrix, are presented in Table 2. Technological properties of the mixed powders were: theoretical and apparent densities, filling relative density, filling porosity and flowability. These properties necessary for the next step of pressing are presented in Table 3.

Table 2. Thermo physical-chemical properties of the elemental powders.

Element	Atomic radius (nm)	Melting point (^{0}C)	Theoretical Density (g/cm^3)	Crystal structure	Atomic percent	Weight percent HEA	Weight percent HEC
Al	0.143	660.5	2.70	BCC, FCC	20	10.84	10.42
Cr	0.128	1860	7.19	BCC	20	20.94	20.52
Fe	0.127	1538	7.87	FCC, BCC	20	22.48	22.06
Mn	0.127	1246	7.21	BCC	20	22.12	20.90
Ni	0.125	1455	8.91	FCC	20	23.60	23.20
C	0.143	3700	2.10	HCP	0	3.0	2.92

Table 3. Technological properties of HEA and HEA/Gr.

Material	Theoretical density (g/cm^3)	Apparent density (g/cm^3)	Filling relative density (%)	Filling porosity (%)
HEA	7.11	2.76	38.82	61.18
HEA/Gr	7.17	2.35	32.77	67.23

The theoretical densities of the mixed powders (HEA and HEC) were calculated with the equation:

$$\rho_m = \%Al\ \rho_{Al} + \%Cr\ \rho_{Cr} + \%Fe\ \rho_{Fe} + \%Mn\ \rho_{Mn} + \%Ni\ \rho_{Ni} + \%Gr\ \rho_{Gr} \quad (1)$$

where theoretical density values for each component were taken from table 2.
The apparent density of the mixed powders was determined under the condition of SREN IS0 3923-1/2008 for flowing powders (density > 1.3g /cm^3). The values for the filling compactation (the filling relative density) of the mixed powders were calculated with the formula:

$$C_f = \frac{\rho_a}{\rho_m} \text{ x } 100\ , [\%] \quad (2)$$

Filling porosities of the mixed powders was calculated with relation:

$$P_f = 100 - C_u. \quad (3)$$

XRD characterization was performed for the high entropy composite (HEC) before the milling process (control sample), after 20 hours of milling (HEC2) and after 40 hours of milling (HEC4): HEC sample contains peaks of pure elements generated by the individual powders contained in the charge mixture (figure 1). After 20 hours of milling several solid solution phases are formed and no elemental peaks are recorded any more (figure 2). The structure is composed of 36% BCC type A2/B2, 29.7% A12 complex type α-Mn, 17.8% BCC type A2 and 16.6%FCC type A1 phases. By comparing the XRD results between the control sample (mixed powders) and 40 hours alloyed sample it was noticed that the diffraction peaks drastically decrease (figure 3).

The results are consistent with those obtained by Sicong Fang and co-authors [14], that found BCC and FCC phase after 38 and 42 hours of milling.

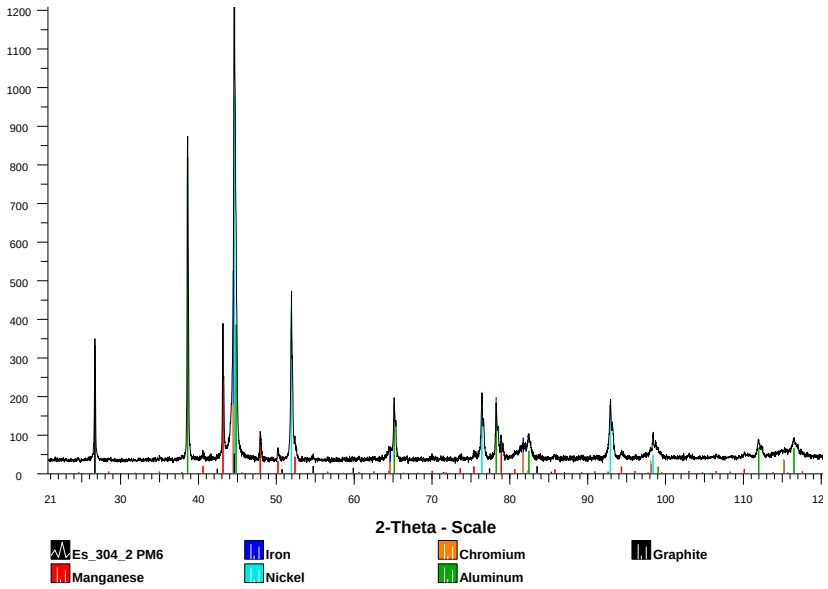
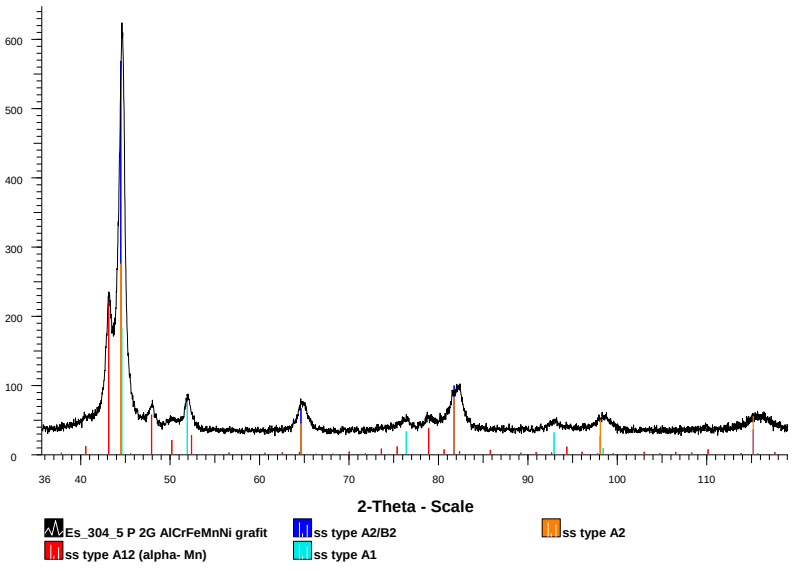


Figure 1. XRD pattern of HEC control sample (0 hours).



Compound Name	PDF References	S-Q (%)
sstype A12 (alpha- Mn)	03-065-3159	29.7
sstype A2/B2	03-065-4899	35.9
sstype A1	03-065-2865	16.6
sstype A2	00-006-0694	17.8

Figure 2. XRD patterns of HEC2 (20 h).

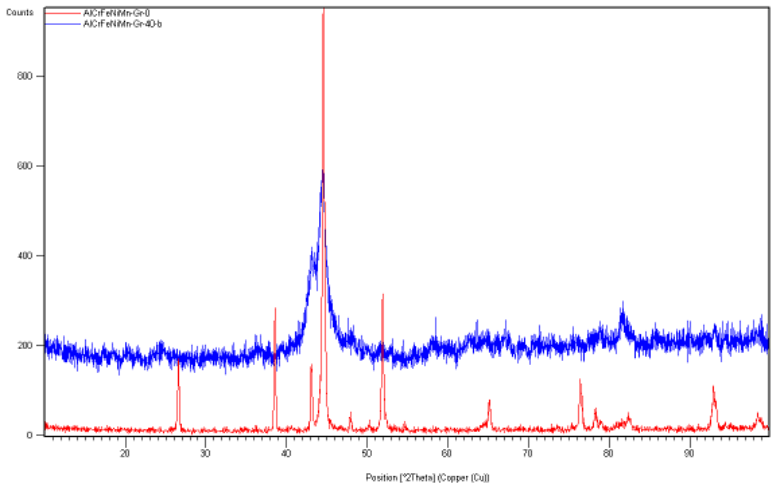
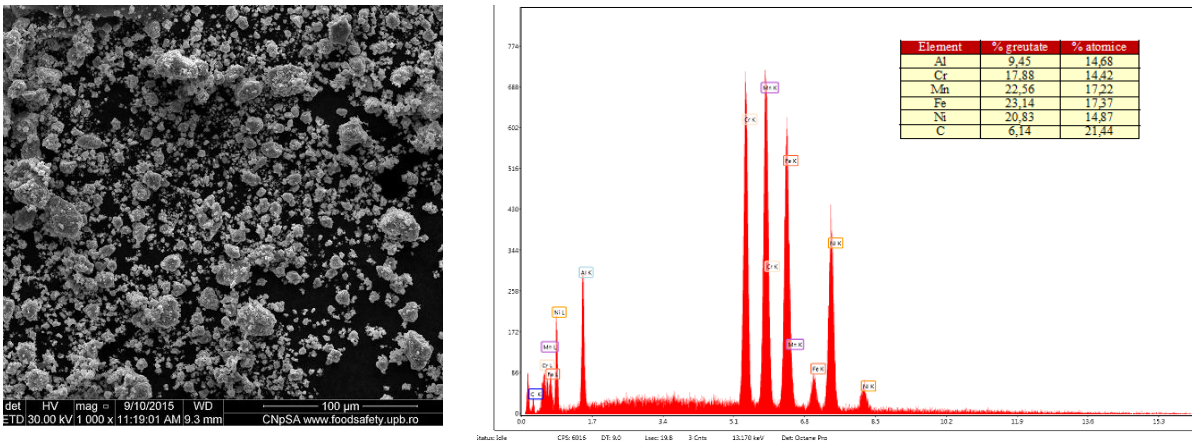


Figure 3. XRD patterns of HEC control sample (0 h - red line) and HEC alloyed 40 h (blue line).

The SEM images and quantitative EDAX analysis of the HEC alloyed for 40 hours, which was chosen as the base material for subsequent pressing and sintering operations, are presented in figure 4.



(a) (b)

Figure 4. SEM image (a) and EDAX spectrum and quantitative analysis (b) of the HEC alloyed for 40 h.

It is noticed that after 40 hours of mechanical alloying the HEA particle sizes were much reduced due to the high energy milling, having dimensions in the nanometric scale.
The 40 h mechanically alloyed samples were pressed and sintered to achieve final desired shape.
In figure 5 and 6 the variation for the density and porosity of the sintered samples is revealed. The density increases with the sintering process. The graph shows that the highest density improvement was obtained for the sample marked HEC4.
It is noted that after sintering the composite porosity decreases. This is a good thing considering that for self-lubricating bearings the porosity value must be 30-40%.
Figure 7 reveals the SEM image of HEC consolidated tablet, having a fairly high degree of compaction, with a quite large densification capacity (around 70%).

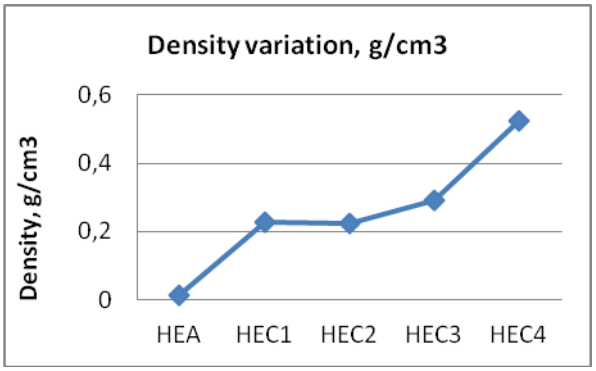


Figure 5. The difference density between pressed and sintered samples

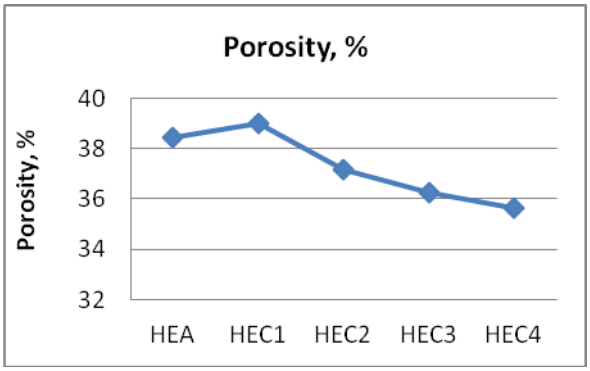
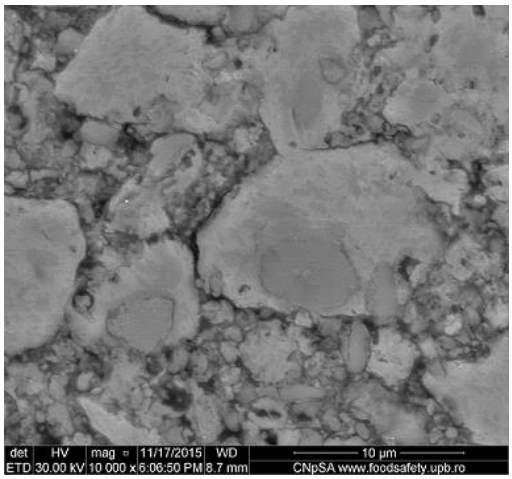


Figure 6. The porosity variation for sintered samples



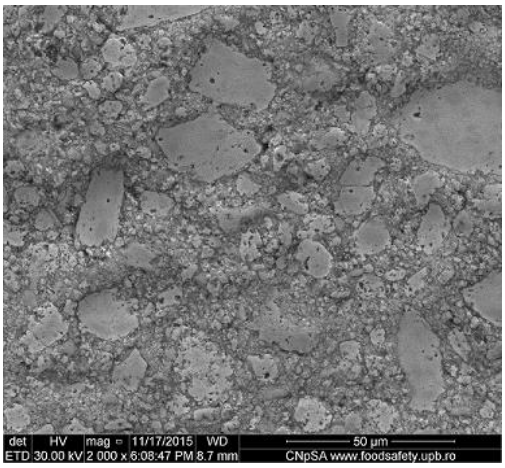


Figure 7. SEM images of HEC alloyed 40 h after sintering at different magnification.

4. Conclusions

AlCrFeMnNi high entropy alloy and AlCrFeMnNi/Gr composite were prepared by mechanical alloying. Characterization of alloy and composite specimens, provided at different milling times, revealed that the alloying process starts after 15 hours and completes after 40 hours. The 20 hours milled specimen presents a structure formed of simple (BCC - A2/B2, BCC - A2 and FCC - A1) and complex solid solutions (BCC - A12). Phase identification is rather difficult to be obtained in the 40 hours milled specimen, due to the drastic reduction in the diffraction peaks and the increase in detection noise. The SEM - EDAX analyses showed that after 40 hours of milling the obtained particles have homogeneous composition and nanometric sizes. The apparent density and porosity of pressed and sintered samples showed optimum values for the specimen milled 40 hours. Due to its advanced properties the mechanically alloyed HEA composite represents a good candidate material for self-lubricating bearings.

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