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Structural Evolution of AlCrFeNiMn/Graphite During Mechanical Alloying from 5 to 40 Hours

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Abstract

High entropy alloys proved to be materials having high hardness and good mechanical properties as well as corrosion resistance. We obtained high entropy alloy consisting in 5 elements to be used as matrix for a composite material. As a reinforcing material we used graphite particles in order to impose some autolubrication properties. We designed this material for bearing used for hot rolling. We realized a series of experiments to assess the microstructure and alloying degree after 5, 15, 20, 25 and 40 hours milling. The powder characterization was realized in order to establish the best parameter for pressing and sintering. The results showed that the powders became nanosized starting from 25hmilling and became completely alloyed at 40h milling.

INTRODUCTION

During the last years, mechanical alloying technique has been more often approached due to the good homogenous chemical distribution and near net shape technology provided by the respectively process [1, 2, 3]. Chao Wang, Wei Ji and Zhengyi Fu obtained simple structured solid solution after 30 h of milling, with a grain size of less than 20 nm while B.S.Murty et al. succeeded to obtain a HEA with BCC structure and grain size of approximately 10 nm [4, 5, 6]. Due to the combinations of composition and process for producing HEAs and each HEA having a particular microstructure and properties to be identified and understood, the research work is versatile and provides a lot of opportunities [7, 8]. High entropy alloys have the tendency to form simple solid-solution structures, with single phase crystal structures. HEAs present sluggish diffusion and severe lattice distortions, which have a major effect on their microstructures and properties. These characteristics have an important impact on determining the remarkable properties of high entropy alloys, such as high hardness and strength, high resistance to anneal softening, high resistance to corrosion, oxidation and wear, good magnetic and electric capabilities, which make HEAs suitable for structural and functional applications. The main characteristic of these alloys is their capability to retain their properties at high temperatures.

Mechanical alloying (MA) is a ball milling process of high-energy which can lead to the obtaining of simple and stable microstructures which present a better homogeneity compared to other non-equilibrium synthesis methods. The MA method presents some advantages compared to the melting-casting route, such as room-temperature processing and the increase of the solid solubility with good homogeneity, especially in the case of multi-element alloy systems which have major differences in the melting points. Moreover, the mechanical alloying process can also produce a nano-crystalline structure, which has a beneficial effect on the improvement of the mechanical properties of these metallic materials.

Mechanical Alloying (MA) implies high energy milling of powder mixtures which are deformed and weld repeatedly during the treatment. This processing method had advantages over other manufacturing processes, such as obtaining composite powders with special characteristics, solid state diffusion processes between the material particles, increasing contact surface of the processed elements and diffusion activation between elements. MA being a commonly used solid state processing route for advanced materials machining, in recent years, the interest in processing HEAs by this technique has increased. According to specialized literature this method provides advantages over other techniques by giving HEAs formed by MA and consolidated by spark plasma sintering (SPS) more homogenous and stable nanocrystalline microstructure, good densification and high strength, widening the application of these materials. This processing route is expecting to reduce the costs of HEAs production [9,10,11].

This paper aims to assess the microstructure and the alloying degree for the high entropy composite AlCrFeNiMn/Gr. The further processing of this composite depends on the homogeneous structure and

a good microstructure. We tried to determine the smallest alloying time in order to further process this composite to be used in different bearings for roll mills.

MATERIALS AND METHOD

High purity metallic powders of Al, Cr, Fe, Ni, Mn were used to be mechanically alloyed, under argon atmosphere, in a high speed planetary ball mill. N-heptan acts as PCA to avoid cold welding as well as to prevent the alloy from oxidizing. Steel vials and balls were used. The chosen milling times for this alloy were 5, 10, 15, 20, 25 and 40 hours. We extracted samples and performed test to see when the powder is completely alloyed. The speed used was 300rpm.The ball to powders (BPR) ratio was 8:1.
The influence of milling time was studied on the microstructure using electronic microscopy and diffraction. The samples were analyzed with a FEI Quanta 3D FEG operating at 20-30 kV, equipped with an energy dispersive X-ray spectrometer (EDS).The powders were characterized in terms of particle sizes, flow rate, average diameter, and bulk and tapped density were calculated. For powders grain size characterization was used a RETSCH size analyzer. The phase structure of the samples was determined by X-ray diffraction characterization XRD experiments were carried out in XPert Pro Panalytical instrument. Prior to mechanical alloying we characterized the samples and we calculated a mean diameter for the powder used and the alloyed samples and we analyzed the un-milled sample, homogenized for 1 hour, to have a comparison due to the lack of data in this field.

RESULTS AND DISCUSSIONS

The powder used for these experiments were high purity elemental powders, with an average diameter of 63 micrometers, having particles of different shapes. The raw material was placed in stainless steel vials, after sieving and N-heptan was added, the vial was sealed and the argon introduced. After the milling the powder has a grey colour and as we can see in the above microstructure the particles dimensions were drastically reduced.
The microstructures of the high entropy composite material are shown in figure 1. The EDS mapping of the elements for the 40h milled powder and the homogenized powder are shown in figure 2 and 3.
Mapping indicates a homogeneous alloying elements distribution for the alloyed sample. The sample was alloyed after 40h of milling. After 25h the results indicates still un-homogeneous mixtures remained in the high entropy composite material. The alloying degree is necessary to be complete to further process the powder into a finite product.
The diffraction pattern for the analyzed samples is shown in figure 4. We calculated VEC for the high entropy alloys obtained after 5h, 15h, 20, 25 and 40h milling to evaluate the amount of FCC and BCC phase present in the microstructure.

The values were calculated with the formula [12]:

$$VEC_{AlCrFeNiMnGr}=\Sigma c_i(VEC)_i \ (i=1\text{-}6) \qquad (1)$$

The results are presented in table 1:

Milling time (h)	VEC
5	7.2
15	7
20	7.1
25	6.98
40	6.82

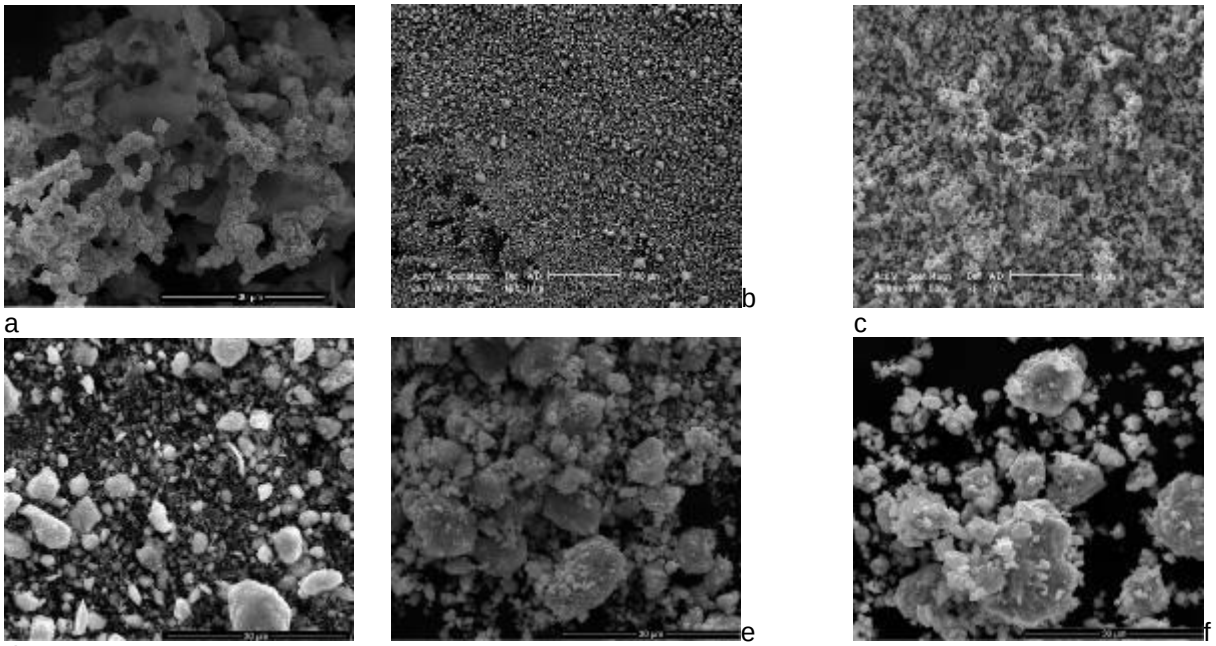

Figure 1. SEM image of AlCrFeNiMn/Gr high entropy composite for sample a) 1(0h), b) 2(5h),c) 3(15h), d) 4(20h), e) 5(25h) and f) 6(40h)

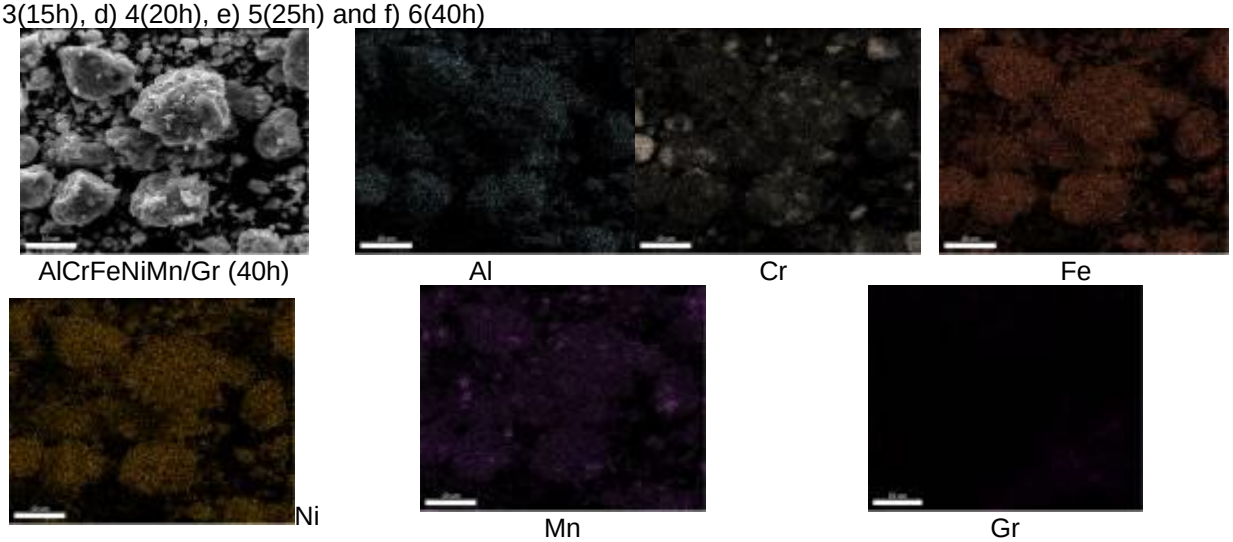

Figure 2. Mapping of the alloying elements for AlCrFeNiMn/Gr high entropy composite milled for 40h

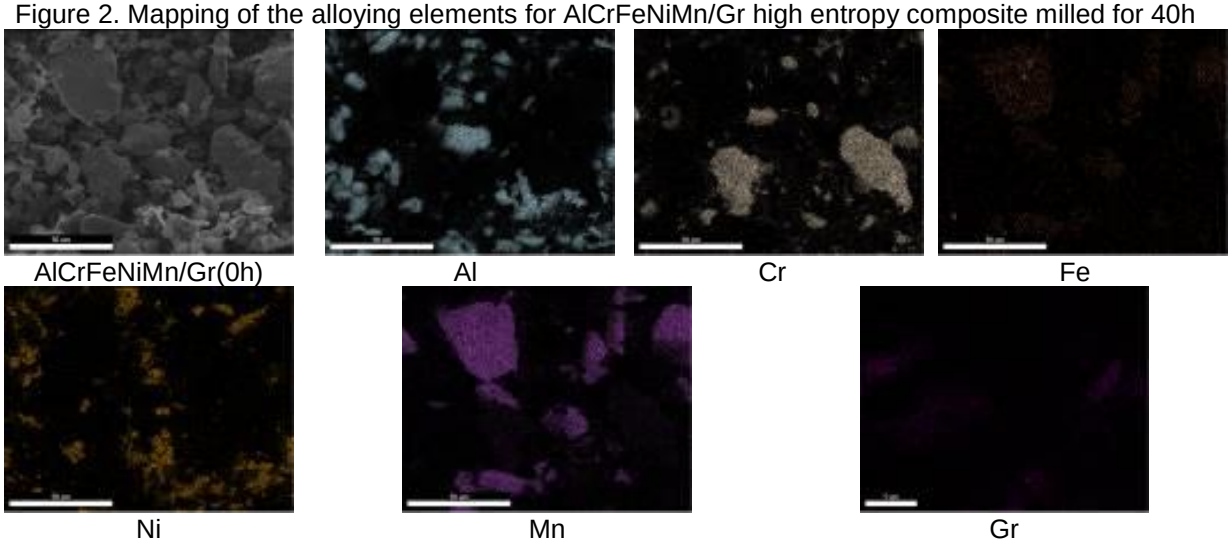

Figure 3. Mapping of the alloying elements for AlCrFeNiMn/Gr homogenized powder, un-milled (0h)

IF the VEC value is more than 8 than the probability for FCC to appear is maximum. If VEC value is less than 6.87 the probability of BCC phase to appear is maximum as Guo et al established [13]. The

values obtained for 40h milling show a decrease of the VEC indicating the FCC transforming to BCC phase. The BCC phase is more likely to produce high hardness of the material but also the mixture with FCC provides a good wear resistance for the material.

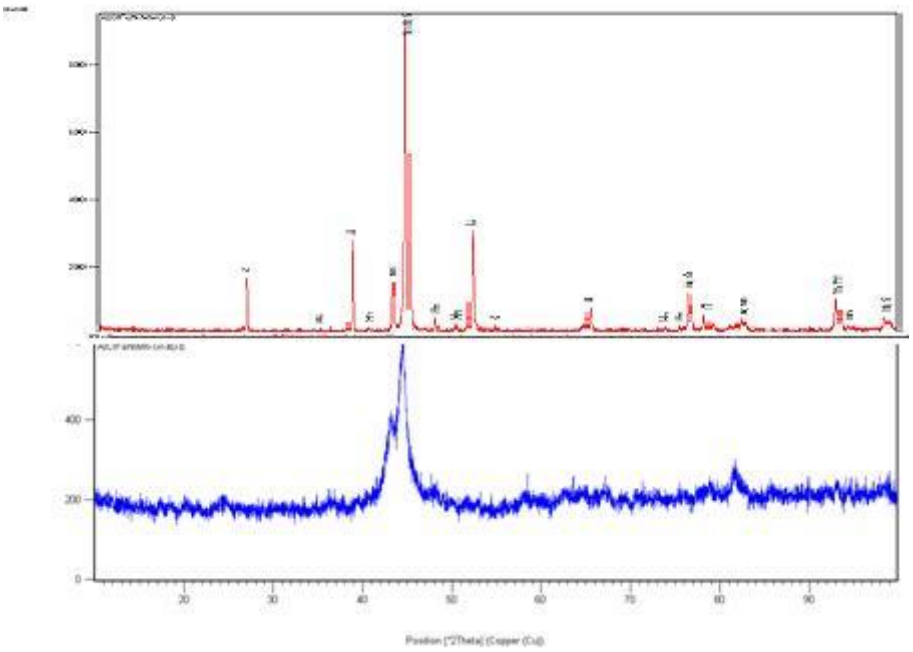

Figure 4. Diffraction pattern for AlCrFeNiMn/Gr high entropy composite at 0h (homogenized sample) and 40h milling (completely alloyed sample)

XRD pattern reveal that throughout the milling process, the decrease in intensity, peaks broadening and its subsequent disappearance may results from several factors: refined crystal size and high lattice strain.
The crystallite size after different milling time and lattice strain has been calculated with Scherrer's formula [14].

$$\tau = K\lambda/\beta\cos\theta \qquad (2)$$

where

τ is the mean size of the ordered (crystalline) domain which may be equal to the grain size

K is the shape factor having a value close to unity, typically 0.9 but can vary function the crystal shape

Λ is the X rays wave length

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;

θ is the Bragg angle

This formula is used to calculated crystallite size for the milled samples. We can see the evolution of the crystallite dimension, decreasing constantly with the milling time increasing.
In table 2 the crystallite size (CS) and lattice strain (LS) of AlCrFeNiMn/Gr are calculated with milling time.

Table 2. **Milling time (h)**	**CS(nm)**	**LS(%)**
5	80	0.09
15	70	0.11
20	32	0.17
25	31	1.57
40	29.2	3.51

CONCLUSIONS

The AlCrFeNiMn/Gr composite was processed by mechanical alloying in order to obtain a material suitable for a bearing for hot rolling, with high corrosion resistance and high wear resistance at high temperature.
The graphite role is to lubricate the composite making them suitable for hot roll mill applications, graphite having a very good influence on lubrication properties, as well as the ability of this material to be pressed in a strong compact. The graphite particles added to the high entropy alloy matrix improved the milling process preventing cold welding of the particles and improving homogeneity.
The purpose of this paper was to determine the appropriate milling time to see when the completely alloyed composite is obtained.
The literature is offering different milling times, usually around 60h and our experiments established that we obtained fully alloyed composite material after 40h.
The input of graphite could improve milling due to its lubrication properties.
The composite obtained was investigated by SEM and EDS and XRD and the results revealed a good structure for the composite that could be further processed by pressing and sintering.

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