Mechanics and Mechanical Engineering
Vol. 21, No. 2 (2017) 415–424

# Synthesis and Characteristization of High Entropy Alloy (CrMnFeNiCu) Reinforced AA6061 Aluminium Matrix Composite

R. K. Prabakaran
*Goverenment Industrial Training Institute*
*Tiruchirappalli- 620014, Tamil Nadu, India*

A. Naveen Sait
*Department of Mechanical Engineering*
*Chendhuran College of Engineering & Technology*
*Pudukkottai-622 507, Tamil Nadu, India*
*naveensait@yahoo.co.in*

V. Senthilkumar
*Department of Production Engineering*
*National Institute of Technology*
*Tiruchirappalli- 620 015, Tamil Nadu, India*

Received (10 February 2017)
Revised (12 March 2017)
Accepted (13 April 2017)

Quinary High Entropy Alloy (HEA) system consists of Cr-Mn-Fe-Ni-Cu elements were prepared though powder metallurgy route. With varying wt. % of above prepared HEA powder as reinforcements, two different (10% and 20%) A6061 aluminium matrix composites were produced. Sinterablity of the composite powders was evaluated with different sintering time and temperature. The XRD results of HEA confirmed that the solid solution possess both FCC and BCC phases. Density, hardness and compressive strength of the fabricated composite were measured to evaluate the effect of HEA reinforcement. SEM micrographs of the composites were evaluated for the structure and to find the distribution of reinforcement particles.

*Keywords*: composites, HEA, AA6061, powder metallurgy.

## 1. Introduction

Metal matrix composites (MMCs) are well known engineering materials due to their excellent properties such as, high specific strength, superior mechanical and tribological properties, for which, they are replacing their monolithic alloys in the various structural and other applications. Two major techniques, liquid phase and solid phase methods are being used to fabricate MMCs [1]. Powder metallurgy route is a well–known solid state fabrication technique which overcomes the problems such as poor wettability, pores, voids and low density rose in liquid state technique (casting).Many researches are still in progress on MMCs to enhance their properties for making them a perfect-suitable material for various applications [2].

Aluminium based metal matrix composites (AMMCs) are one of the widely used MMCs for structural applications in aerospace, automotive and chemical industries due to their high strength-to- weight ratio, high elastic modulus, wear resistance and corrosion resistance which make them more attractive especially for structural components [3]. In general, aluminium based composites are fabricated by reinforcing particles like, $Al_2O_3$, SiC, $B_4C$, TiC, $TiB_2$ and graphite to enhance mechanical properties. However, reinforcement agglomerations, particle fragmentation followed by porosity, cracking are major drawbacks of ceramic reinforced composites [4]. Moreover, a mismatch in thermal expansion coefficient between matrix and ceramic reinforcements leads to deteriorate the composite properties. Furthermore, only some specific properties can be improved by particular ceramic particles reinforcement. Hence, a new system of reinforcement, metallic elements as reinforcement is being investigated in recent years to conquer the above drawbacks and improve the structural properties [5]. Instead of single metal, a multi component system as a reinforcement is highly proposed because of their excellent mechanical, thermal and corrosion properties. These multi–component systems were termed as 'high entropy alloy (HEA)' by yeh et al. [6].

HEA is differ from conventional alloys with respect to the presence of principal elements. In conventional alloys, there is one or rarely two base elements present whereas HEA consists of minimum of five and maximum thirteen principal elements. Equimolar or nearly equimolar elements which has less difference in atomic radii are used to form HEA to maintain single phase solid solution and control the phase change or transition [7]. The large number of components in equi-atomic proportions increases the configuration entropy as maximum, as well as contribution to Gibbs free energy which stabilizes the solid solution phase. Minimize the enthalpy and maximize entropy will lead to form single solid solution. Even though, the alloying elements present in HEA have difference in coefficient of thermal expansion, and there will be no phase transition take place like ceramic composites which will lead to strengthen the composite [8]. In HEA, intermetallic and other complex compounds are not formed like alloys. This can be attributed to lower Gibbs energy with high entropy that suppress the segregation or ordering tendency which leads to form stable solution [9]. HEA is still in earlier stages hence a detailed investigation is needed. Beneficial properties of HEA system such as high strength and hardness, better resistance to corrosion, oxidation, wear and fatigue with good thermal stability, magnetic properties, highly stable at elevated temperature were reported elsewhere [10]. AA2024 reinforced with (AlCuMg) ternary HEA particulate composite exhibited improved mechanical properties in terms of resistivity, hardness, and tensile-yield strength with increased reinforcement content [11]. AlCoNiCrFe-HEA reinforced Cu matrix composites were fabricated by Powder Metallurgy (PM) route which showed enhanced compression and yield strength than metallic glasses. In this alloying system, there was no intermetallic system found during sintering process and also grain growth was also not occurred [12].

In the present investigation, Cr-Mn-Fe-Ni-Cu quinary stocktickerHEA system as reinforcement and AA6061 alloy as matrix materials were used to produce the composite through powder metallurgy route under different sintering temperature and time. XRD and stocktickerSEM techniques were used to analyze the phase formation and powder morphology respectively after mechanical alloying. Properties such as density, hardness and compressive strength were calculated to evaluate the effect of stocktickerHEA reinforcement on Al alloy matrix.

## 2. Experimental details

AA6061 aluminium alloy as a matrix material was reinforced with HEA for preparing composites. The constituent elements of AA66061 is shown in Table 1 were carefully weighed and mixed in high energy planetary ball mill for 5 hrs for matrix alloy fabrication.

**Table 1** Chemical composition of AA6061 alloy

| Elements | Mg | Si | Fe | Cu | Zn | Ti | Mn | Cr | Al |
|---|---|---|---|---|---|---|---|---|---|
| Standard (wt.%) | 0.8-1.2 | 0.4-0.8 | Max. 0.7 | 0.15-0.4 | Max. 0.25 | Max. 0.15 | Max. 0.15 | 0.04-0.35 | Balance |
| Selected (wt.%) | 0.8 | 0.6 | 0.7 | 0.275 | 0.25 | 0.15 | 0.15 | 0.175 | Balance |

### 2.1. *Synthesis of HEA*

The reinforcement used in this study was HEA which consists of quinary elements of equiatomic wt.% as shown in Table 2. The elements for this reinforcement were carefully selected based on the atomic radius. If the difference between the radii of elements is less, the formation of single solid solution during alloying will be better while synthesize those elements. The reinforcing elements such as Cr, Mg are brittle whereas other elements, Fe, Ni, and Cu are ductile. The ductility of the system is predominant for improving the formability regarding structural application whereas brittle elements used in this system enhancing the strength and hardness.

High energy planetary ball mill was used for synthesis of HEA elements. The weighed powders are milled in a stainless steel vial with Ø16 mm steel balls at 150 rpm speed with toluene as a process control agent. The powder to ball ratio was 1:10. During ball milling process, element present in the vial are subjected to high impact force which lead to fragmentation of brittle materials and flattening of ductile materials. Moreover, the milling process involved repeated cold welding, fracturing and re-welding which forms homogeneous-single/multi solid solution of powders. The formation of alloying was examined with the regular interval of 10 hrs, 20 hrs and 40 hrs using X-ray diffraction technique. Based on the XRD results, 40hrs milled HEA was chosen as reinforcement to fabricate the AA6061-HEA composites.

Then 10% and 20% of HEA powders (40 hrs. milled) were mixed with AA6061 matrix in ball mill for 5 hrs.The morphology of composites powders was examined using scanning electron microscopy (SEM). This mixture was then cold compacted using hydraulic press at a constant load of 650 MPa and the compacted sample was

**Table 2** High entropy alloy (HEA) system

| Elements | Atomic radii (Å) | Atomic weight (amu) | Weight % |
|---|---|---|---|
| Chromium (Cr) | 1.28 | 52 | 18.227 |
| Manganese (Mn) | 1.39 | 54.94 | 19.258 |
| Iron (Fe) | 1.26 | 55.85 | 19.577 |
| Nickel (Ni) | 1.24 | 58.69 | 20.661 |
| Copper (Cu) | 1.28 | 63.55 | 22.277 |

in the form of cylindrical shape with the dimensions of 12 mm in dia and 12 mm in height. Molybdenum disulfide ($MoS_2$) was used as lubricant to avoid wall friction between die and punch. The samples were sintered at two different temperatures of $560^o$C and $600^o$C, for two different soaking times of 1 hr and 2 hrs under argon atmosphere. The sintered composite samples were subjected to suitable mechanical polishing for hardness measurement. Wilson Wolpert micro hardness tester was equipped to measure the hardness of fabricated composites with a constant load of 500 g at 10 s dwell time. The compressive strength of the composites was calculated using FIE servo controlled universal testing machining at a uniform ram speed of 2 mm per minute.

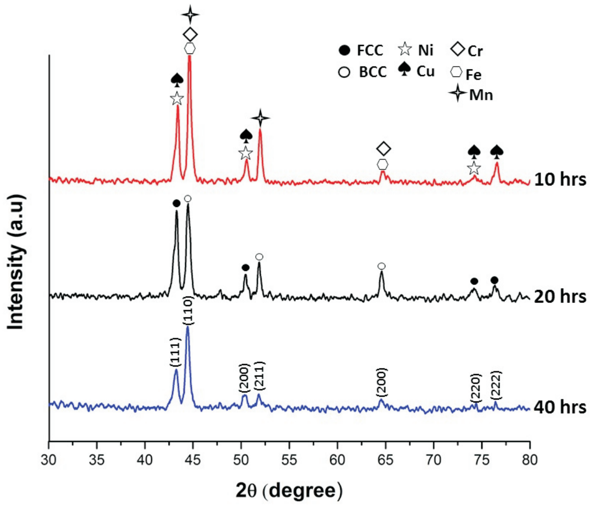

**Figure 1** X–ray diffraction of HEA powders milled at different time

## 3. Results and discussions

### 3.1. *X-ray diffraction analysis of HEA*

Fig. 1 shows the X-ray diffraction pattern of HEA-reinforcement material (CrMnFeNiCu) milled for various duration. It was clearly identified that the milled HEA system consist of both FCC and BCC phase solid solution irrespective of milling time.

Mixing FCC (or BCC) elements with high (or low) valence electrons in equal atomic ratio does not always guarantee as it will form a FCC (or BCC) solid solution. The formation of FCC+BCC structure depends on the structure of constituent elements. If (VEC $\geq 8$) would form stable FCC solid solution and (VEC $< 6.87$) could lead stable BCC solid solution. Only a few compositions have been reported that result in a single–phase solid solution. The XRD results showed that the present HEA system has dominant FCC system with less BCC phase. This is due to the transition metals system CrFeMnNi [2], would lead to form FCC alloys. The phase formation of alloying system is shown in Tab. 3.

**Table 3** Phase formation in CrMnFeNiCu HEA system

| Phase | Composition | Mole fraction |
|---|---|---|
| FCC | Ni–Mn–Fe | 0.384 |
| BCC | Cr-Mn | 0.232 |
| FCC | Cu | 0.200 |
| BCC | Fe | 0.184 |

Fig. 1 it was found that the intensity of peaks changes along with the milling time. When the milling time is increased the peak intensity decreased and peak broadening occurred. This is ensured that the reduction of crystallite size and increment of lattice strain of the HEA which is calculated from Scherrer's equation. From Table4, the 40hrs milled HEA system has least crystallite size and high lattice strain which is used to fabricate the AA6061 composite. It was reported that after 40 hrs of HEA there is no significant change in lattice strain.

**Table 4** Crystallite size and lattice strain of HEA

| Milling time | Crystallite size (nm) | Lattice strain |
|---|---|---|
| 10 hours | 44.67 | 0.0022 |
| 20 hours | 22.42 | 0.0051 |
| 40 hours | 15.69 | 0.0063 |

### 3.2. *Powder characterization*

Fig. 2 shows the morphology of matrix, 40 hrs milled HEA powder used as reinforcement and aluminium composite powders of varying percentage of HEA reinforcement10% and 20% respectively. From Fig. 2a, it is observed that the constituents of AA6061 are evenly distributed among the aluminium powder. Fig. 2b shows HEA powder after 40 hrs milling. The alloying elements are flattened due to the presence of more ductile materials as discussed in section 2.1. The size of the powder is also reduced due to the increased milling time. The flattened particles enhanced the binding capability with the matrix alloy. The distribution of reinforcing HEA particles in the matrix is ensured from Figs. 2c and d. Smaller reinforcing particles can be easily accommodated by the AA6061 matrix which may induce better bonding between them and reduce the porosity as a result.

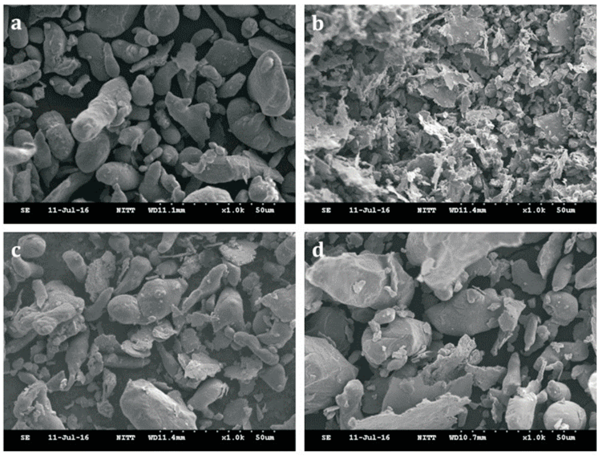

**Figure 2** SEM micrograph of: a) AA6061, b) 40hrs milled HEA, c) AA6061 + 10% HEA, d) AA6061 + 20% HEA

### 3.3. *Density*

The density of AA6061 matrix and HEA reinforcement were calculated as 2.77 g/cc and 7.566 g/cc respectively.The density of the composites after sintering is provided in Table 5. The change in density percentage is shown in Fig. 3. From the table 5 and Fig. 3, it is noticed that the density of composites is increased along with the soaking temperature and time. When the soaking time and temperature are increased the density of matrix and composite is found to be increasing. About 1.5% of density increment is noticed at 600$^o$C of 2 hrs soaking period.

**Table 5** Density (g/cc) of composites after sintering

| System | Theoretical density | 560$^o$C 1hr | 600$^o$C 1hr | 560$^o$C 2hrs | 600$^o$C 2hrs |
|---|---|---|---|---|---|
| AA6061 | 2.77 | 2.657 | 2.669 | 2.684 | 2.694 |
| AA6061 + 10% HEA | 3.249 | 3.048 | 3.052 | 3.055 | 3.059 |
| AA6061 + 20% HEA | 3.729 | 3.452 | 3.463 | 3.491 | 3.501 |

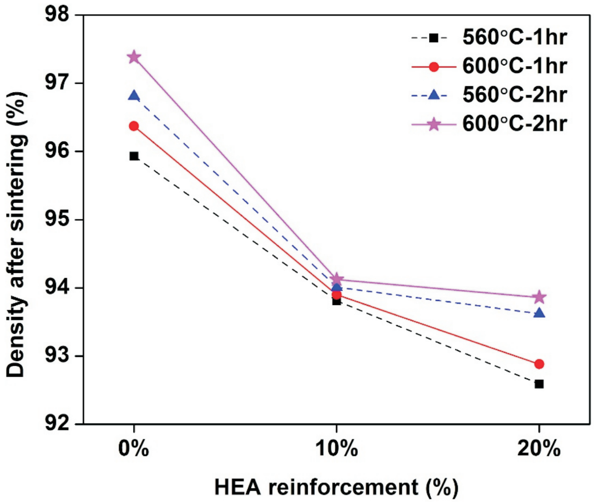

**Figure 3** Density variation of composites

From the Fig. 3, it is clearly seen that the matrix material AA6061 has highest density for given sintering temperature and time. Absence of reinforcement particles and better diffusion of aluminum particles due to sintering temperature (recrystallization temperature of AA6061 is ≈ $250^oC$) can be attributed for its higher density. However, the densities of composites were seemed to be less due to addition of HEA–reinforcement particles. About 3.5% density reduction in composite was found as compared to matrix. Constant load during compacting is insufficient to compress the HEA materials which failed to make good bonding with the matrix material, hence less density was achieved. Moreover, reinforcement particles generated voids which increased the porosity (Fig. 4) of composite material compared to matrix. But, the sintering process increased the density of the composites by reducing porosity. From the Fig. 4, it was found that the porosity of the composite was increased with the addition of reinforcing particles compared to matrix material. However, 35% and 5-10% of reduction in porosity was found in matrix and composites respectively when soaking time and temperature was increased.

### 3.4. *Microhardness*

The microhardness of the samples were measured with 10 trials at different places and the average value was recorded. The average hardness of AA6061 matrix was measured as 59-73 in Vickers scale after sintering for given conditions. Fig. 5 shows the microhardness of the matrix and composites at different conditions. Sintering has significant effect on the hardness of the given material. When both sintering time and temperature were increased the hardness values of the samples also increased. ≈18% of improvement of hardness was found when the matrix material was sintered at $600^oC$ for 2 hours. As discussed earlier, reduction in porosity, formation of good bonding among the elements of AA6061 alloy and sufficient load promoted to better hardness values. Hard metallic particles present in HEA enhanced the hardness of the composite material. Even though both 10% and 20% HEA reinforced composites held less density, they showed higher hardness values than matrix material. This is due to the reason that HEA particles posses higher hardness values than matrix material. Moreover, the smaller particle size of reinforcement increases the strain energy at the boundary which promote better bonding at the interface. The uniformly distributed HEA particles in the matrix offer more restriction to the deformation during the indentation of hardness measurement.

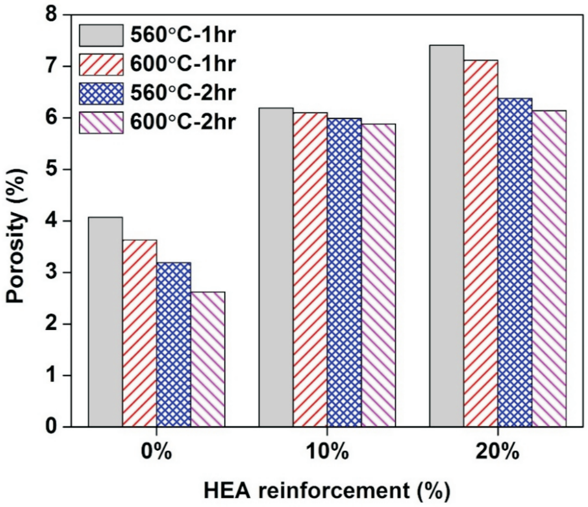

**Figure 4** Porosity of composites after sintering

### 3.5. *Compressive strength*

The compressive strength of the AA6061 alloy and HEA reinforced aluminium composites was illustrated in Fig. 6. It was observed that the compressive strength of both matrix and composite were increased with the soaking process. Improved bonding, elimination of voids and porosity can be attributed for 18-35% enhancement of compressive strength of the matrix material. Addition of reinforcement particles with the matrix also improved the compressive strength of the composites. Formation of stable BCC solid phase, improved hardness and good mechanical properties of the HEA elements increased the compressive strength of the composites. However, 20% HEA reinforced composite exhibited lesser strength than 10% reinforcement. Higher amount of reinforce particles increased the strain at the boundary which initiate the crack formation that resulted in failure of the material.

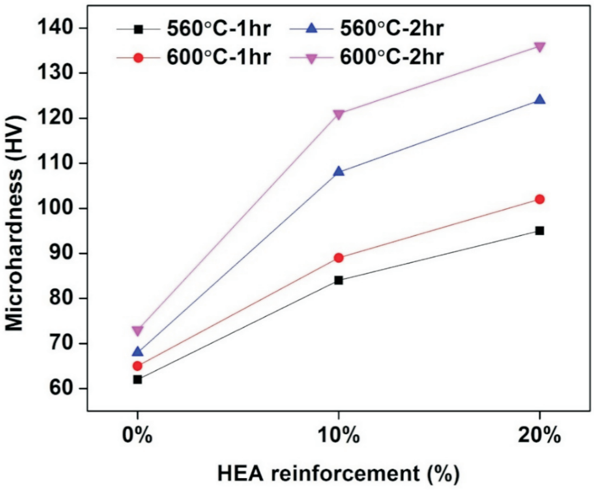

**Figure 5** Microhardness of the composites

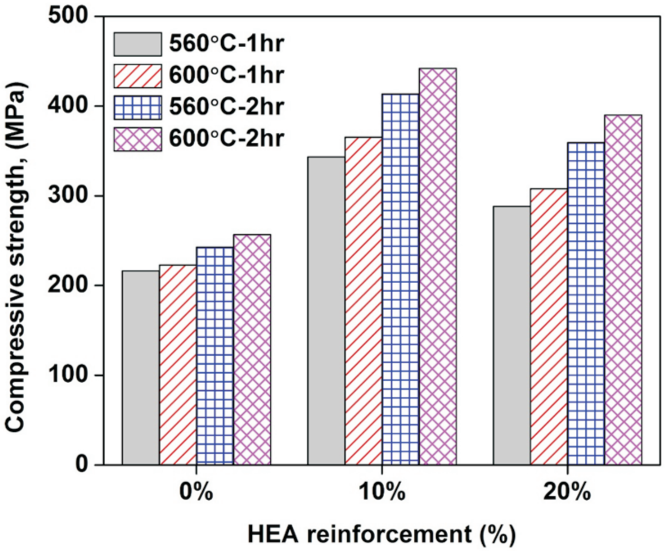

**Figure 6** Compressive strength of the composites

## 4. Conclusions

Equiatomic CrMnFeNiCu high entropy alloy was successfully fabricated through mechanical alloying and used as reinforcement in AA6061 matrix to produce composite. Powder SEM and XRD analysis were carried out for morphology analysis. Density, hardness and compressive strength were evaluated and the following broad conclusions are made.

1. XRD analysis showed that the selected HEA system consists of both FCC and BCC solid phases. 40 hrs milled HEA powder has less crystallite size and more lattice strain.

2. Flattened powder particles of HEA were observed from the SEM micrograph.

3. Densities of the composites were reduced upto 3.5% compared to matrix material. HEA reinforced AA6061 exhibited improved microhardness values when compared to AA6061 matrix.

4. 10% HEA reinforcement has higher compressive strength than 20% reinforcement. The sintering temperature and time have significant effect on the properties of HEA reinforced aluminium alloy composites.

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