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Synthesis and Microstructural Characterization of Nanostructured High Entropy Alloy

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Abstract*: *High entropy alloys (HEAs) are formed by mixing of five or more elements with equal or large proportions. In the current study Al0.3Cr-FeNiCo0.3Si0.4 nanostructured high entropy alloy (HEA) is produced by means of mechanical alloying. The as-received elements in the powder form were processed in a high-energy ball mill with a ball-to-powder ratio (BPR) 15:1 and a speed of 300 rpm. Two Al0.3Cr-FeNiCo0.3Si0.4 alloy samples were produced with the same variables except milling time where alloy A was milled for 1 hr while alloy B was mechanically alloyed for 25 hr. Milling time is increased from 1 to 25 hr to allow the formation of the solid solution of the elements and the synthesis of high entropy alloy. The as-received powders were examined by Apreo field emission gun scanning electron microscope (FEGSEM). The distribution and dissolution of the elements in the produced alloys was examined using energy dispersive spectroscopy (EDS) attached to a high resolution scanning electron microscope system (FGSEM).

Keywords* : *Al-Cr-Fe-Ni-Co-Si Alloy, Nanostructured High Entropy Alloy, Mechanical Alloying, Microstrucre Analysis.

I. INTRODUCTION

Recently, materials engineers are showing more interests towards high entropy alloys (HEAs) because of their specific microstructures and enhanced properties [1-3] which provide promising industrial and engineering uses. HEAs are novel group of alloys designed through mixing of minimum five alloying elements with almost equi-atomic concentrations. The content of each component lies in the range of 5% - 35% [4]. The conventional alloys, on the other hand, have one major component with content more than 50% as a principle alloy composition. In these alloys, the anticipated microstructure and expected performance can be attained by minor alloying additions such as iron-, aluminum-, copper- and magnesium-based alloys [5].

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The current studies illustrate that HEAs are simply a nanostructured solid-solution which avoid the formation of undesired precipitates and second phase intermetallic particles [6, 7]. The influence of iron (Fe) content on the microstructural variation and mechanical behavior of $Al_{25}Ti_{25}Ni_{25}Cu_{25}$ and $(AlTi)_{60-x}Ni_{20}Cu_{20}Fe_x$ (x=15, 20) HEAs were Investigated [8]. Heptanary nanocrystalline AlCoCrCuNiFeZn HEA was developed through solid state mechanical alloying (MA) [9]. This newly developed alloy had produced single phase alloy with a body centered cubic (BCC) structure which revealed enhanced uniformity in the attained microstructure. Novel $AlFeCuCrMg_x$ (x=0, 0.5, 1, 1.7 mol) HEAs were synthesized through mechanical alloying (MA) [10]. It was found that this novel alloy exhibited a BCC structure as a major phase and a FCC structure as a minor phase in AlFeCuCr and $AlFeCuCrMg_{0.5}$ HEAs. In addition, it was concluded that the addition of magnesium resulted in improving the development of BCC single phase structure. The variations in microstructure and the corresponding changes in mechanical behavior of $Al_{0.5}CrFeNiCo_{0.3}C_{0.2}$ twinned HEA was investigated [11]. This novel alloy was produced through MA and consolidated by spark plasma sintering technique. It was found that after 38 h of MA a supersaturated solid solution of face centered cubic structure was formed. The manufacturing and mechanical behavior of AlCoNiCrFe HEA inserted in copper matrix was investigated using MA [12]. It was observed that this HEA was successfully formed after 24 h MA and it revealed nanoscale structure even after consolidation without forming unfavorable intermetallic particles. The impact of nickel-to-chromium ratio on the variation of microstructural and corresponding changes in mechanical behavior of $Ni_xCoCuFeCr_{2-x}$ HEAs was investigated where x =1.0, 1.2, 1.5, and 1.8 mol [13]. These HEAs were synthesized by MA and spark plasma sintering. The FCC single phase structure was observed to increase with augmenting Ni/Cr ratio while BCC structure was noticed to reduce as a result of Cu atoms segregation and/or addition of Cr atoms. The effect of iron on the microstructure and mechanical response of $Al_{0.5}CoCrFe_xNiTi_{0.5}$ HEA was studied [14]. The addition of Fe was observed to stabilize the FCC phase structure so that the addition of Fe supported the development of FCC phase. The microstructure and mechanical response of AlCoFeMoNiTi alloy was investigated [15]. This HEA was manufactured using two techniques MA and arc melting; the HEA produced by MA displayed 15% extra improvements in the results in comparison to arc melting. The influence of cobalt and titanium additions in $Al_{0.75}FeNiCrCo$ HEA was investigated [16].

These alloys were manufactured through solid state MA followed by spark plasma sintering technique. The sintered $Al_{0.75}$FeNiCrCo HEA was observed to display improved strength which was attributed to several active strengthening mechanisms. Al_xCoCrFeNi ($0 \leq x \leq 2$) HEAs were developed and the variations in microstructure and resultant mechanical properties were investigated in the deformed and as-cast conditions. It was reported that FCC single phase structure was formed as a result of adding Al content up to 0.375 fraction. In addition, FCC/BCC dual phases were observed to form when adding Al in the range of 0.5 - 0.75 fraction.

According to several studies, the incorporation of aluminum (Al) particles in the multicomponent high-entropy alloying concepts would enhance the performance of products [18]. Hence, based on this information and several discussions made in the literature section, Al0.3CrFeNiCo0.3Si0.4 high entropy alloys (HEAs) system has been selected for the present study [19]. In addition, the influence of silicon (Si) content in HEAs has not been carried out by any other researcher much [20,21]. Further, to manufacture the proposed HEAs, the well-known solid state route of mechanical alloying is chosen as the formation of nanostructured is easily obtained. Two $Al_{0.3}$Cr-FeNi$Co_{0.3}Si_{0.4}$ HEA samples were produced with the same variables except milling time where alloy A was milled for 1 hr while alloy B was mechanically alloyed for 25 hr. Milling time is increased from 1 to 25 hr to allow the formation the HEA. This article will present only the microstructural characterization of the processed alloys.

II. EXPERIMENTAL PROCEDURE

High-purity elemental powders of aluminum, chromium, iron, nickel, cobalt and silicon were used as starting powders for ball milling process. The powders reveal a purity > 99.9% and average particle size < 44 μm (-325 mesh). The designed alloy composition of the synthesized Al0.3Cr-FeNiCo0.3Si0.4 alloy is shown in Table 1. The elemental powders were ball milled by Pulverisette 5/2 classic line type ball mill. Two 250 ml size vails and 10 mm diameter balls made of tungsten carbide were used as grinding media. The pre-mixed powders were milled for 1 hr (alloy A) and 25 hours (Alloy B) with BPR of 15:1 and a speed of 300 rpm. The ball milling was performed in an absolute ethanol with purity >99.99%. Milling was achieved in the sequence of 15 min forward cycle, stop for 15 min, reverse cycle for 15 min and another stope for 15 min, this complete cycle is recurrent to attain 1 hr and 25 hr of continuous milling in alloy A and alloy B, respectively. Thereafter, the ball milled alloys in the form of powders were dried under vacuum for microstructural examination. Green compacted samples were produced by MTS universal test machine where the powders were compressed in H13-steel die with 15 mm inner-diameter and with applying a load of 1100 MPa. The shape and size of the powders of the starting elements were examined by Apreo field emission gun scanning electron microscope (FEGSEM). Overlay maps of elemental distribution in produced Al0.3Cr-FeNiCo0.3Si0.4 alloys in powder and green form were analyzed using energy dispersive X-ray spectroscopy (EDS) attached to FEGSEM. EDAX-TEAM advanced program was used for qualitative and quantitative analysis the processed samples microstructure. The average size of the powder particles of the synthesized Al0.3Cr-FeNiCo0.3Si0.4 alloys were measured using a dynamic laser light scattering (Malvern instrument).

Table- I: Chemical composition and milling time of the synthesized Al0.3Cr-FeNiCo0.3Si0.4 alloy

Alloy Code	Milling duration	Chemical Composition, wt.%					
		Al	Cr	Fe	Ni	Co	Si
A	1 hr	7.5	25	25	25	7.5	10
B	25 hr						

III. RESULTS AND DISCUSSION

Figure 1 displays the shape and size of the starting powders where aluminum has almost rounded shape; cobalt displays agglomerated-spherical particles; chromium shows platelet morphology; iron has fine spherical shape; nickel shows a rounded morphology; and silicon reveals an acicular fragment. The average particle size of the starting powders is less than 44 μm (-325mesh).

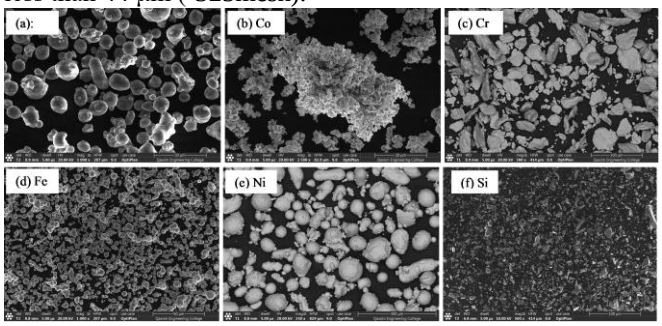

Fig. 1.The size and shape of the starting powders: (a) Al; (b) Co; (c) Cr; (d) Fe; (e) Ni; and (f) Si

The Z-average particle size of the fabricated alloys in the powder form was found 1427nm and 364.3nm for alloy A and alloy B, respectively. Figure 2 represents the distribution of particle size versus intensity% for the processed alloys. Table 2 shows a summary of the particle size analysis where for alloy A, one main peak is observed with an average size of 888.8±170.8nm at peak intensity of 100%. On the other hand, alloy B revealed bimodal size distribution as seen in Figure 2 where the main peak was found at peak intensity of 89.9% with an average particle size of 386.2±202.1nm. From Table 2, it was observed that ball milling of the initial powders mixture resulted in reducing the particle size from 44 micron to 1427nm in case of alloy A. An additional reduction in particle size of alloy B to 364.3nm was recorded due to the prolonged milling to 25 hr. In addition, PDI (Polydispersity Index) of alloy A and alloy B was found 0.523 and 0.364, respectively, as an indication to the dispersity of the particles on a narrow size distribution.

Alloy A showed bimodal size distribution with a relatively larger value of PDI (0.523) which refers to a wider particle size distribution range of this alloy. On the other hand, with increasing milling time, alloy B displayed a monodisperse size distribution with PDI of 0.364,

as indication to the uniformity of the size of powder particles and the dispersion of the powders on a narrow size range.

Table- II: The particle size results of alloy A and B.

Alloy Code	Peak #	Size (d.nm)	% Intensity	Standard Deviation (d.nm)
Alloy A	Peak 1	888.8	100	170.8
	Peak 2	0.000	0.00	0.000
	Peak 3	0.000	0.00	0.000
	Z-Average (d.nm) = 1427, PDI = 0.523			
Alloy B	Peak 1	386.2	89.8	202.1
	Peak 2	4336	10.2	1036
	Peak 3	0.000	0.00	0.000
	Z-Average (d.nm) = 364.3, PDI = 0.5230.364			

Figure 3 illustrates the elements distribution of $Al_{0.3}Cr$-$FeNiCo_{0.3}Si_{0.4}$ alloy in the powder form after ball milling for one hour (alloy A). Figure 3(a) shows the overlay map of all elements in $Al_{0.3}Cr$-$FeNiCo_{0.3}Si_{0.4}$ alloy where it may be noticed that there is no uniformity of elements distribution and no dissolution observed. These remarks are related to the short milling time which is insufficient for forming HEA. The distribution of aluminum is shown in Figure 3(b); silicon in Figure 3(c); chromium in Figure 3(d); iron in Figure 3(e); cobalt in Figure 3(f); and nickel in Figure 3(g).

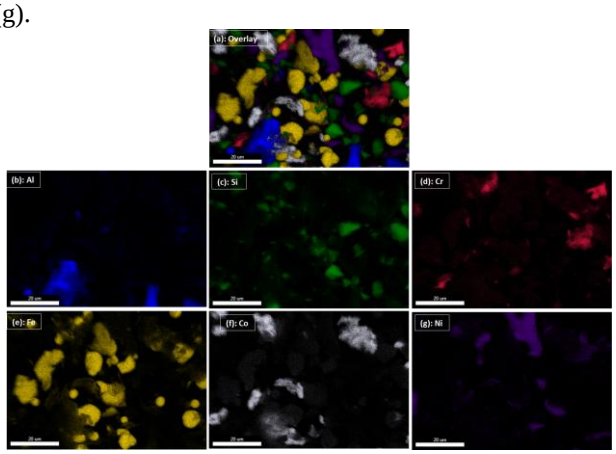

Fig. 2. Elements distribution in Al0.3Cr-FeNiCo0.3Si0.4 alloy in its the powder sample: (a) an overlay map of all elements; (b) Al; (c) Si; (d) Cr; (e) Fe; (f) Co; and (g) Ni distribution in the selected powder sample.

IV. CONCLUSIONS

In the current study $Al_{0.3}Cr$-$FeNiCo_{0.3}Si_{0.4}$ nanostructured high entropy alloy (HEA) is successfully synthesized by mechanical alloying after applying high-energy ball mill for 25 hr, BPR 15:1 and a speed of 300 rpm. The processed $Al_{0.3}Cr$-$FeNiCo_{0.3}Si_{0.4}$ mixtures for 1 hr produced nonhomogeneous mixture of the elemental powders without actual alloying due to the short milling time. The average particle size of alloy A was found 1427 nm while longer milling time to 25 hr (alloy B) resulted in an additional reduction in particle size to 364.3 nm. The homogeneity and dissolution of the elements in $Al_{0.3}Cr$-$FeNiCo_{0.3}Si_{0.4}$ alloy was observed to improve with increasing the milling time. Alloy B which processed for 25 hr was found to form HEA as confirmed from the elemental mapping and EDS analysis in the processed powder and green compacted samples.

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