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Phase formation in mechanically alloyed $Al_xCoCrCuFeNi$ ($x = 0.45, 1, 2.5, 5$ mol) high entropy alloys

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ABSTRACT

Alloying behavior and phase transformations in $Al_xCoCrCuFeNi$ ($x = 0.45, 1, 2.5, 5$ mol) multi-component high entropy alloys that are synthesized by mechanical alloying were studied. Two FCC phases along with a BCC phase were formed in $Al_{0.45}CoCrCuFeNi$ and AlCoCrCuFeNi, while a single B2 phase was observed in higher Al containing alloys $Al_{2.5}CoCrCuFeNi$ and $Al_5CoCrCuFeNi$. DSC analysis indicates that BCC phase present in the alloys could be Fe–Cr type solid solution. A detailed analysis suggests that two melting peaks observed during DSC in lower Al containing alloys can be attributed to that of Cu–Ni and Fe–Ni FCC solid solutions. The BCC phase disappears in $Al_{0.45}CoCrCuFeNi$ and AlCoCrCuFeNi at high temperatures during DSC. However, $Al_5CoCrCuFeNi$ retains its B2 structure despite of heating in DSC. Further, phases present in these alloys retain nanocrystallinity even after exposure to high temperatures. A critical analysis is presented to illustrate that solid solution formation criteria proposed for high entropy alloys in the literature are unable to explain the phase formation in the present study of alloys. Besides, these criteria seem to be applicable to high entropy alloys only under very specific conditions.

1. Introduction

Since the time of their evolution in 2004, multi-component high entropy alloys (HEA) attracted a considerable attention by many research groups across the world due to the nature of phases formed in these alloys and their encouraging properties [1,2]. In general, it is anticipated that complex phases or intermetallics may form when alloying is attempted with more number of elements. However, in contrast, these equi-atomic multi-component alloys are observed to form solid solutions with simple crystal structures, which is the origin for a widespread interest in this class of alloys.

$Al_xCoCrCuFeNi$ ($x = 0–3$ mol) is a well-studied system, and thus it is pertinent to provide an overview of the previous studies on this system to bring out the issues relevant to phase formation. All the literature reports dealing with $Al_xCoCrCuFeNi$ system are presented in Table 1 [2–15], and a brief discussion on Table 1 is given below. Table 1 presents the alloy composition, the processing route and phases formed in the processed stage. A close inspection of Table 1 suggests that the widely studied processing route for this alloy system is casting [2–7,11–15] and few reports deal with mechanical alloying (MA) [8,9], magnetron sputtering [10], and splat quenching [14] routes. A couple of studies have been carried out by Zhang et al. [8,9] that deal with MA of AlCoCrCuFeNi. It is interesting to note that for the same composition, as cast microstructures vary from one study to another one. For example, for the same equi-atomic composition AlCoCrCuFeNi, the cast alloys were reported to exhibit different microstructures ranging from two to five phases [2–4,13,14]. It is also important to note that with an increase in Al content in this alloy system, these alloys were reported to transform from FCC to BCC/B2 or FCC + BCC structure [2–4,15]. Although, there have been some studies using casting route to deal with influence of Al amount on the phase formation in this alloy system [2–4], there are no detailed MA studies to investigate the influence of Al content on phase formation in $Al_xCoCrCuFeNi$. Clearly, based on the above discussion, no consistent picture emerges with reference to influence of Al content on phase formation in this alloy system.

In addition, owing to problems associated with casting such as segregation and inhomogeneity, MA has been chosen as the synthesis route in the recent studies [8,16–18]. Mechanical alloying also decreases the tendency to ordering and leads to extended solid solubility [19]. Thus, as compared to casting route, MA is anticipated to give simple crystal structures for the same composition. Further, MA route is also established to facilitate the formation of

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Table 1
Previous studies that are reported in the literature on HEA alloy system $Al_xCoCrCuFeNi$.

S. No	Composition	Processing route	Phases	Reference
1	$Al_{0.3}CoCrCuFeNi$	Casting	FCC	[2,4,15]
2	$Al_{0.5}CoCrCuFeNi$	Casting	FCC	[2–6,15]
		Casting and forging	FCC + BCC	[6]
		Casting, homogenized and furnace cooled	2 FCC + BCC	
3	$Al_{0.8}CoCrCuFeNi$	Casting	FCC + BCC + Second FCC(Neutron diffraction)	[7]
4	AlCoCrCuFeNi	Casting	2 FCC + 2 BCC	[3]
		Casting	FCC + BCC + B2	[2]
		MA-60 h	Supersaturated BCC	[8,9]
		Magnetronsputtering	FCC + BCC + amorphous	[10]
		Casting	FCC + BCC	[4,11,12]
			(Fe,Cr) BCC + NiAl B2 + FCC	[13]
		Splatquenching	B2	[14]
		Casting	FCC1, B2 precipitate, L12precipitates (Curich), AlNi B2, Cr–Ferich BCC	
			B2 + FCC	[5]
5	$Al_{1.3}CoCrCuFeNi$	Casting	B2 + FCC	[2]
6	$Al_{1.5}CoCrCuFeNi$	Casting	B2 + FCC	[2,4,15]
7	$Al_2CoCrCuFeNi$	Casting	FCC + BCC	[2]
			FCC + B2	[3]
8	$Al_{2.5}CoCrCuFeNi$	Casting	FCC_{minor} + B2	[2,4,15]
9	$Al_3CoCrCuFeNi$	Casting	B2	[2,4,15]

nanocrystalline HEA [8,16–20]. In addition, calorimetric studies to understand the phase transformation in $Al_xCoCrCuFeNi$ system are very limited [8,15] in the literature.

Above discussion dealing with Table 1 and a critical analysis of the literature suggest that it is interesting to carry out a detailed study on the effect of varying amounts of Al on phase formation and phase transformation in $Al_xCoCrCuFeNi$ system processed by MA route. Consequently, a systematic study was carried out in the present study to understand the phase formation of mechanically alloyed $Al_xCoCrCuFeNi$ (x = 0.45, 1, 2.5, 5 mol) multi-component HEA. In the present study, it is shown that MA produces different phases as compared to that by casting route for the same composition. In addition, it is also shown that the criteria developed by Zhang et al. [21] for phase formation in HEA are neither a necessary nor a sufficient condition to explain the phase formation in these $Al_xCoCrCuFeNi$ HEAs.

2. Experimental details

The elemental powders of Al, Co, Cr, Cu, Fe, and Ni of purity greater than 99% with mesh size of 200–300 were mechanically alloyed using Fritsch Pulverisette-P5 high energy planetary ball mill. The compositions studied were $Al_xCoCrCuFeNi$ (x = 0.45, 1, 2.5, 5 mol). The vials and balls of WC were used with toluene as the milling medium, and the ball to powder weight ratio was taken as 10:1. The milled powders were collected at regular intervals of 20 min, 5, 10, 15 and 20 h to study phase formation using X'Pert Pro Panalytical X-Ray diffractometer (XRD) with Cu K_α radiation. The 20 h MA powders were characterized using scanning electron microscope (SEM) in back scattered electron (BSE) mode to observe the particle size and morphology. The composition of the alloys was characterized using energy- dispersed spectroscopy (EDS) of SEM to observe chemical homogeneity. The 20 h MA powders were heated in a NETZSCH differential scanning calorimeter (DSC) till 1480 °C in Ar atmosphere at a heating rate of 20 K/min to understand the thermal stability of the phases formed.

3. Results

The XRD patterns, SEM micrographs, and DSC curves reported here are representative of the specific compositions in the present study. Further, the homogeneity of the processing route was verified by conducting more than two measurements of XRD and DSC for all the alloys studied.

3.1. Phase formation during mechanical alloying

In the present study, $Al_{0.45}CoCrCuFeNi$ and $Al_5CoCrCuFeNi$ are the compositions with minimum and maximum Al content. Fig. 1a represents the XRD patterns of $Al_{0.45}CoCrCuFeNi$ as a function of milling time. With increase in milling time, Al dissolves and its peaks completely disappear after 10 h of milling. Cu also dissolves to some extent as indicated by the decrease in its peak intensity in relation to the other peaks. A detailed analysis of this XRD pattern reveals that the alloy consists of three phases after 20 h of milling, two FCC phases (designated as F_1 and F_2) and a BCC (designated as B) phase.

Pseudo-Voigt function was used for fitting XRD peak profile and Si standard was used for correcting instrumental broadening. Crystallite size and lattice strain for milled samples were calculated using Williamson–Hall (W–H) method. As the highest intense peaks of F_1 and BCC phases overlap with each other, phase fractions (X_{phase}) are obtained from (220) peak of FCC phases and (211) peak of BCC phase. Phase fraction of F_1 phase is calculated by Equation (1).

$$X_{F1} = I_{F1}^{(220)} / \left(I_{F1}^{(220)} + I_{F2}^{(220)} + I_{B}^{(211)} \right) \quad (1)$$

where, $I_{phase}^{(hkl)}$ is the integrated intensity of XRD peak corresponding to a (hkl) plane. Similarly, phase fractions of F_2 and BCC phases have been obtained. Table 2 shows the phases present after 20 h MA in this alloy, their fraction, crystallite size, lattice strain and lattice parameters. As shown in Table 2, BCC phase is the predominant phase with 56% in this composition of $Al_{0.45}CoCrCuFeNi$. It also has the lowest crystallite size (17 nm) and lattice strain (0.22%) in comparison to FCC phases. The F_1 (FCC) has the largest crystallite size (50 nm) and lattice strain (0.39%) among the three phases. A close observation of the change in the XRD pattern with milling time and the lattice parameter of F_2 phase (0.362 nm) indicates that it seems to be a Cu rich phase (lattice parameter of Cu is 0.3615 nm).

Fig. 1b shows the XRD pattern of $Al_5CoCrCuFeNi$, which clearly illustrates the formation of a single phase, an ordered BCC (B2) phase. It is interesting to note that formation of single B2 phase takes place within 10 h of milling. The (100) superlattice reflection is also visible in the XRD pattern of 10 h milled sample. With increase of milling time, the (100) superlattice reflection gets more intensified till 15 h of milling. Additional milling beyond 15 h did not result in any further change in XRD pattern, and hence XRD patterns up to 15 h of milling are only shown in Fig. 1b. The B2 phase has very small crystallite size (6 nm) and large lattice strain (0.6%) in comparison to the BCC phase observed in low Al containing alloy $Al_{0.45}CoCrCuFeNi$ (Table 2).

Fig. 1c illustrates XRD patterns of all four alloy compositions of $Al_xCoCrCuFeNi$ (x = 0.45, 1, 2.5, 5 mol) after 20 h milling. The XRD