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## PAPER

## Phase evolution and thermal stability of mechanically alloyed CoCrCuFeNi high entropy alloy

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**Abstract**

A CoCrCuFeNi high entropy alloy (HEA) prepared by mechanical alloying (MA) exhibits evolution of two phases, a BCC phase ( $a = 0.287 \pm 0.002$  nm) and a small amount of FCC phase ( $a = 0.362 \pm 0.002$  nm) after 65 h of milling. From the scanning electron micrographs, flaky nature of milled powders and a wide range of particle size (5 to 10  $\mu\text{m}$ ) can be seen. The nanostructure of the crystallites evolved in the 65 h milled powder was analyzed using XRD and selected area electron diffraction techniques. The stability of the 65 h milled powder is studied through *in situ* high-temperature X-ray diffraction (HT-XRD) over a range of temperatures. The as-milled powder is thermally stable up to 623 K, and then the precipitation of the tetragonal (Cr-Co/Fe) based sigma ( $\sigma$ ) phase ( $a = 0.845 \pm 0.002$  nm,  $c = 0.454 \pm 0.002$  nm) occurs. On annealing at 623 K, precipitation of the  $\sigma$  phase started, while on annealing at 1073 K the BCC phase disappears associated with a decrease in the amount of  $\sigma$  phase. Eventually, the FCC phase ( $a = 0.362 \pm 0.002$  nm) appeared to be the stable phase along with a negligible amount of  $\sigma$  phase.

**1. Introduction**

The advent of High Entropy Alloys (HEAs) [1] has broken the paradox that multi-principal element alloys form intermetallic compounds with complex crystal structures. In several cases, it has been verified that multi-component HEAs will result in simple solid solution phases, if processed under appropriate conditions. There is an expeditious increase in the research efforts to design and develop HEAs with improved properties [1–13]. Maximum possible ideal configurational entropy of mixing ( $>1.61R$ ) in these alloys is achieved by mixing five or more elements in equiatomic or near-equiatomic proportion. The high entropy of the alloy system significantly increases the chances of stabilizing a single solid solution phase ( $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$ ). Single phase HEAs hold promise to serve as good base materials for alloy design and development due to solid solution strengthening. In general, all the conventional materials correspond to the region near to terminals of a multicomponent phase diagram; this means that a vast number of possible alloys are unexplored in the central regions of the phase diagrams of multicomponent systems.

A variety of processing routes are adapted to prepare this new class of materials, such as casting, mechanical alloying (MA), and thin film deposition [14]. The casting is the most commonly used route for preparation of the HEAs. Most of the HEAs prepared by casting route show simple solid solutions, while a detailed analysis of the microstructure of the samples thus prepared has shown some segregation in dendritic and inter-dendritic regions [1, 14–17]. The problem of segregation can be avoided by the use of MA [18]. Therefore, its use for the synthesis of HEAs has increased in recent years. Murty *et al* [19] were the first to prepare the nanostructured solid solution of HEAs by MA. Through MA, almost any kind of material can be produced at room temperature [20, 21]. The extended solid solubility of alloying elements plays a vital role during the synthesis of alloyed powders [18]. Due to this extended solid solubility, simple crystal structures are expected for a similar composition compared to casting route. Further, the MA route used to synthesize HEAs facilitates the formation of nanocrystalline phases [9].

The solid solubility of binary alloys is usually predicted by the Hume-Rothery rules, based on the various factors, namely crystal structure, atomic size, the valence electron, and electronegativity. However, the Hume-Rothery rules cannot be used directly for multi-component systems. One can predict the behavior of an element with respect to other elements in the alloy systems based on the enthalpy of mixing for binary subsystems. Large negative deviation in the enthalpy of mixing from the ideality ( $\Delta H_{mix} = 0$ ) favors the formation of intermetallic compounds, whereas positive enthalpy will favor clustering and segregation within the selected alloy systems. Formation of the disordered solid solution takes place for moderate values of enthalpy of mixing. The solubility of one component into other depends on substitutional solid solution forming criteria which in turn control the value of enthalpy of mixing and configurational entropy of mixing. High entropy in multi-principal elemental compositions overcomes the effect of small positive enthalpy of mixing, resulting in the formation of disordered solid solutions. Zhang *et al* [22] have reported that small size difference favors the formation of solid solution. Thus, enthalpy and atomic size factor play an important role along with high configurational entropy in deciding whether the intermetallic, amorphous, or disordered solid solution phase will form.

Among the HEAs, CoCrCuFeNi system has been extensively investigated earlier [14, 23–27]. Al and Ti are generally added to this alloy in varying amounts to study the phase evolution and mechanical properties of the designed systems. Most of the studies on these alloy systems are carried out on as-cast samples [27]. Praveen *et al* [14] and Thangaraju *et al* [27] have studied this system by the MA route. They have reported the presence of the phase after sintering the alloy. However, Thangaraju *et al* [27] have not reported any  $\sigma$  phase formation after sintering. Due to this conflict in the results, it is important to reassess the thermal stability and evolution of the  $\sigma$  phase in CoCrCuFeNi system. In the present context, the thermal stability of the alloy is studied using *in situ* high-temperature X-Ray Diffraction (XRD) technique.

## 2. Materials and experimental procedures

Equiatomic proportion (20 at.%) of above 99.9% purity elemental powders of copper, cobalt, chromium, iron, and nickel were milled in a high-energy planetary ball mill (Retsch PM 400) at room temperature. The MA process was carried out at a speed of 200 rotations per minute (rpm) with a ball to powder weight ratio of 10:1. Tungsten carbide (WC) vials and balls of 10 mm diameter were used for the milling. Toluene was used as the process control agent (PCA) for the wet milling. The powders were collected at every 5 h to study structural evolution with respect to time. Phases, lattice structures, and microstructures of the milled powder were investigated through XRD (Rigaku, 40 kV, 15 mA), transmission electron microscope (TEM, FEI Tecnai G2 T20, 200 kV), and scanning electron microscope (SEM, FEI Quanta 200F, 20 kV), respectively. In-situ phase evolution was studied through high-temperature XRD (Rigaku Smart Lab, 45 kV, 200 mA) with Cu-K $\alpha$  radiation.

## 3. Results and discussion

### 3.1. Empirical method of phase forming rules and the stability of CoCrCuFeNi HEA

In the empirical approach, important parameters such as enthalpy of mixing ( $\Delta H_{mix}$ ), the configurational entropy of mixing ( $\Delta S_{mix}$ ), atomic radius difference ( $\delta$ ) and valence electron concentration (VEC) based on extended Hume-Rothery rules are calculated for the selected alloy system to find out whether it will form a single phase or mixture of phases. The literature on the phase stability of HEAs suggests that these parameters play significant roles in predicting a single phase disordered solid solution. For quinary and higher systems, a single phase solid solution can be expected for  $\Delta H_{mix} < 3.2$  kJ/mol but  $> -11.6$  kJ/mol, while  $\Delta S_{mix} \geq 1.61R$  [10, 28, 29]. Experimental  $\Delta H_{mix}^{ij}$  data are rarely available for many binary alloys. Therefore,  $\Delta H_{mix}^{ij}$  is estimated for binary solutions using the Miedema's model considering electron density changes at the boundary of dissimilar atoms and the work function of pure metals [30]. Formation enthalpy using Miedema's model can be calculated for binary system as

$$\Delta H_{mix}^{ij} = \frac{V_i^{2/3}}{(n_{ws}^{-1/3})_{avg}} [P(\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2] \quad (1)$$

$$(n_{ws}^{-1/3})_{avg} = \frac{1}{2} \left( \frac{1}{(n_{ws}^i)^{1/3} + (n_{ws}^j)^{1/3}} \right) \quad (2)$$

The binary interaction parameters,  $\Omega_{ij}$ , obtained from the calculated mixing enthalpy using Miedema's model are used to estimate the integral molar enthalpy of mixing for multicomponent alloy solutions [5],  $\Delta H_{mix}$ , which is similar to a regular solution model.

**Table 1.** Parameters used in Miedema's model for calculation of mixing enthalpy and binary mixing enthalpy.

Element	$n_{ws}$	$n_{ws}^{1/3}$	$\phi$	V	$V^{2/3}$	$\Delta H_{mix}^{ij}$				
						Co	Cr	Cu	Fe	Ni
Co	5.36	1.75	5.1	6.7	3.55	...	5.5	11	11	3
Cr	5.18	1.73	4.65	7.23	3.74	5.5	...	-4	-1	0
Cu	3.18	1.47	4.45	7.12	3.70	11	-4	...	-1	-7
Fe	5.55	1.77	4.93	7.09	3.69	11	-1	-1	...	-2
Ni	5.36	1.75	5.2	6.6	3.52	3	0	-7	-2	...

**Table 2.** Calculated values of all the parameters which play an important role in phase stability.

Alloy	$\Delta H_{mix}$ (kJ/mol)	$\Delta S_{mix}$ (J/mol/K)	$\delta$ (%)	VEC	$\Delta\chi$
CoCrCuFeNi	2.35	14.40	1.03	8.80	0.09

The mixing enthalpy of a multicomponent alloy consisting of N elements is as follows

$$\Delta H_{mix} = \sum_{i,j>i}^N \Omega_{ij} x_i x_j \quad (3)$$

where  $\Omega_{ij} = 4\Delta H_{mix}^{ij}$  is an interaction parameter for the system  $ij$ ,  $x_i$  is the atomic fraction of the  $i$ th component,  $\Delta H_{mix}^{ij}$  is the mixing enthalpy for the binary equiatomic alloy, which is determined using Miedema's model [31]. The calculated values for mixing enthalpy of the binary subsystems are given in table 1 along with the parameters used for the calculations of enthalpy of mixing for solid solution. The  $\Delta H_{mix}$  value calculated for the quinary HEA (2.35 kJ/mol) is well within the specified range for forming solid solution phase ( $-11.6$  kJ/mol  $< \Delta H_{mix} < 3.2$  kJ/mol) [22]. From table 1, it can be seen that all the binary systems (other than those containing Cu) except Co-Ni have small negative values of enthalpy of mixing, favors formation of solid solution phase.

The configurational entropy of mixing of N-elements can be expressed as follows

$$\Delta S_{mix} = -R \sum_{i=1}^N x_i \ln x_i \quad (4)$$

where  $x_i$  is the atomic fraction of  $i$ th element, R the gas constant. Zhang *et al* [29] defined a parameter arising from the atomic size difference to establish a relationship with solid solubility for multi-component systems.

$$\delta = 100 \sqrt{\sum_{i=1}^n x_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (5)$$

where  $r_i$  is the atomic radius of the  $i$ th element of atomic concentration and  $\bar{r}$  is a weighted average of  $r_i$ , which is given by  $\bar{r} = \sum_{i=1}^n x_i r_i$ . Value of  $\delta \leq 6.6$  favors the formation of simple solid solution [29]. As all the elements are from the 3d transition series, the atomic size difference calculated using the above formula for solid solution forming is equal to 1.03, which is much smaller than 6.6. This also favors the formation of a solid solution. Valence electron concentration (VEC) play a critical role in determining the disordered BCC, FCC, or mixture of two phases forms. For an N component system, the VEC is given [32] by

$$VEC = \sum_{i=1}^N x_i (VEC)_i \quad (6)$$

It has been shown that a single phase FCC solid solution forms for  $VEC \geq 8$ , whereas a single phase BCC solid solution is expected for  $VEC \leq 6.8$  [32]. For intermediate values of VEC, a two-phase mixture of FCC and BCC phases is expected. VEC represents the total number of electrons in the valence band, including the d-electrons. The calculated values of all the parameters, as mentioned above, are given in table 2. Many researchers [5, 9, 28, 33] have pointed out that enthalpy and the atomic size difference play a dominant role in the formation of a solid solution in HEAs compared to the entropy effect. For the system chosen, both these parameters are found to be within a solid solution forming range. In the present context VEC value is 8.80 indicating the possible formation of the FCC phase.

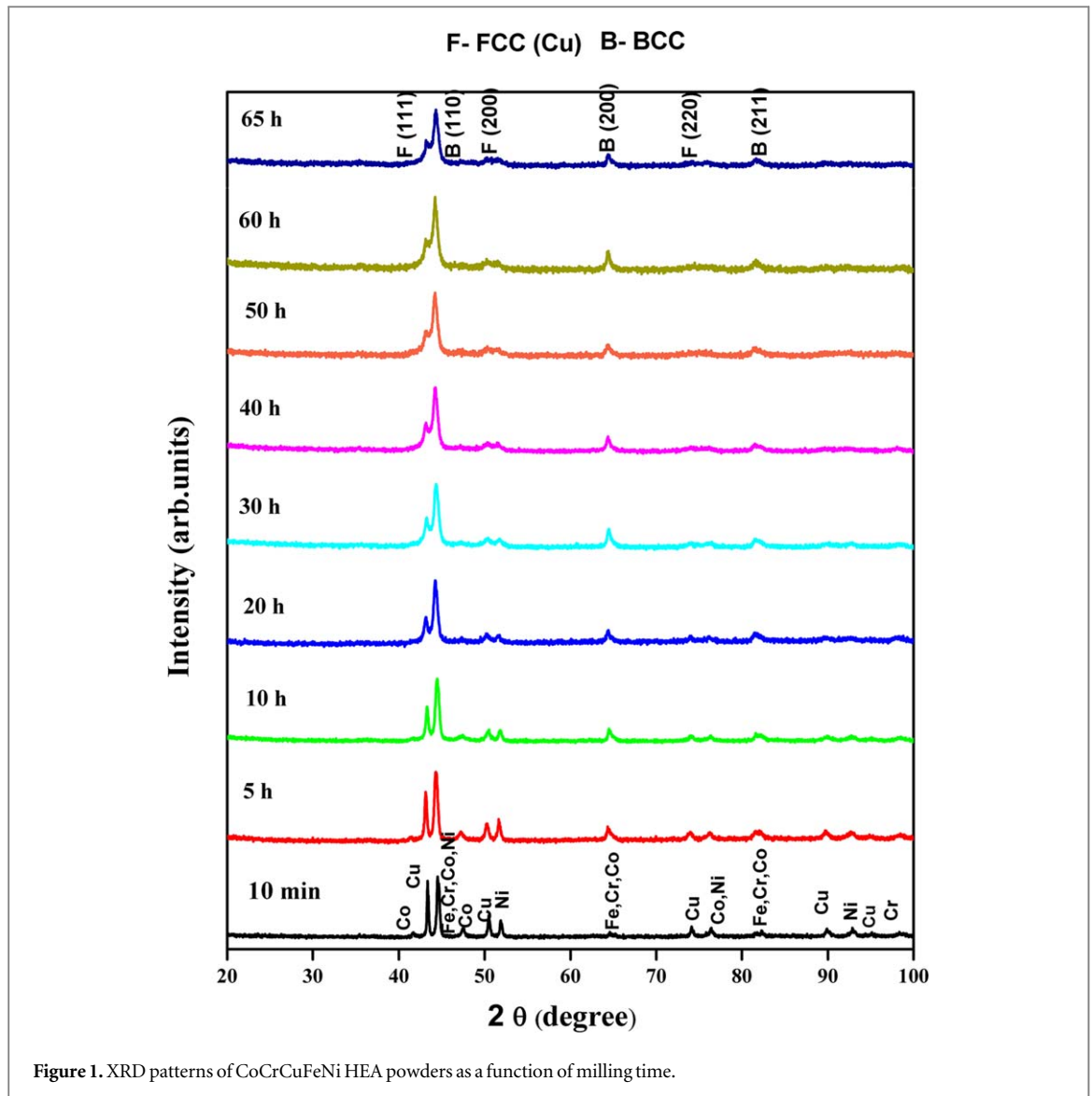


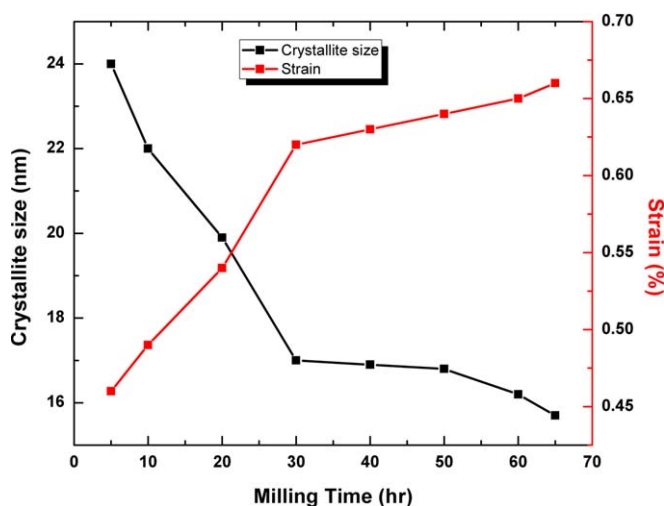
Figure 1. XRD patterns of CoCrCuFeNi HEA powders as a function of milling time.

### 3.2. Characterization of CoCrCuFeNi milled powder

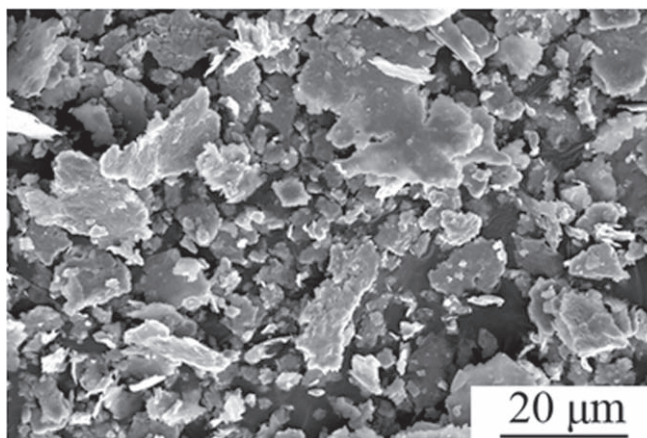
The quinary CoCrCuFeNi HEA was mechanically milled for up to 65 h. Evolution of the phases at regular intervals of milling time has been studied through XRD. The diffraction patterns corresponding to the different milling times are given in figure 1. At the initial blending of powder (10 min.), diffraction peaks corresponding to every constituent element could be observed confirming the presence of all the alloying elements in the starting material. The diffraction intensities of all the constituent elements decrease with broadening of the peaks with an increase in milling time. The peaks intensity corresponding to (100) and (101) planes of Co and (200) plane of Ni reduced significantly after 10 h of milling which disappeared completely by 30 h of milling. It can be seen that most of the peaks lose their identity except those corresponding to Fe/Cr and Cu. As the lattice parameters of the Fe and Cr are very close, peaks corresponding to them overlap. This suggests that a solid solution has formed by the dissolution of Co and Ni in the lattice of Fe/Cr. It is not clear at this stage whether Co and Ni are forced in Fe or Cr host lattice to form BCC phase as lattice parameter of the evolved phase is close to that of Fe as well as Cr. Due to a reduction in the crystallite size and increasing internal strain, there is a significant reduction in the peak intensities of all the higher order reflections. No further changes occur in the diffraction pattern of the powders milled for 50–65 h and correspond to the formation of two-phase structure. Crystallite size and strain have been determined using the Scherrer's method [34], in which, the following equations estimate the peak broadening  $B$  due to crystallite size and internal strain.

$$B_{\text{crystallite}} = \frac{k\lambda}{L\cos\theta} \quad (7)$$

$$B_{\text{strain}} = \eta\tan\theta \quad (8)$$



**Figure 2.** Variation of crystallite size and lattice strain has been shown as a function of milling time. It shows that crystallite size decreases with increases in lattice strain as milling proceed with time.

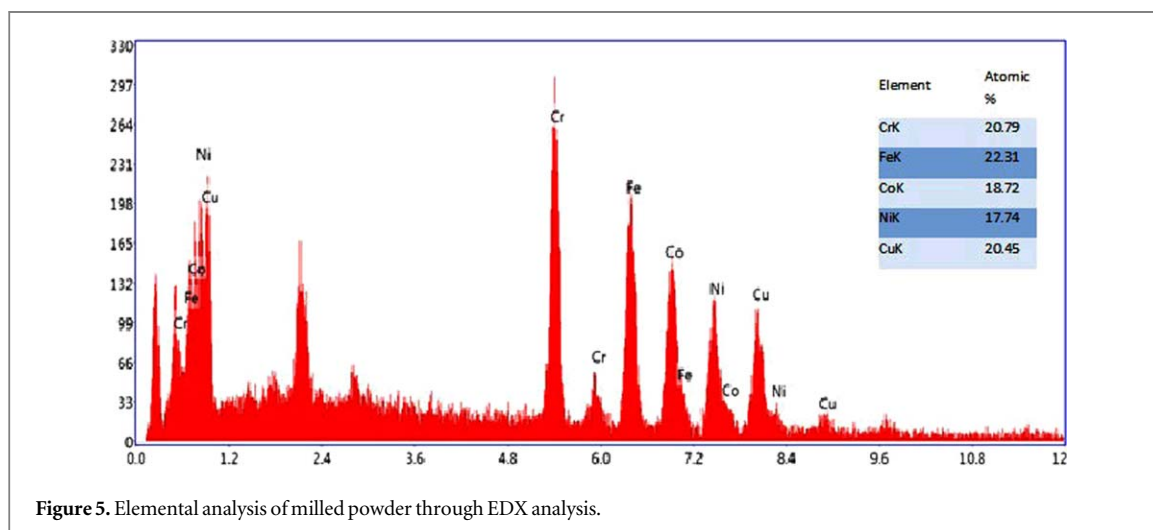
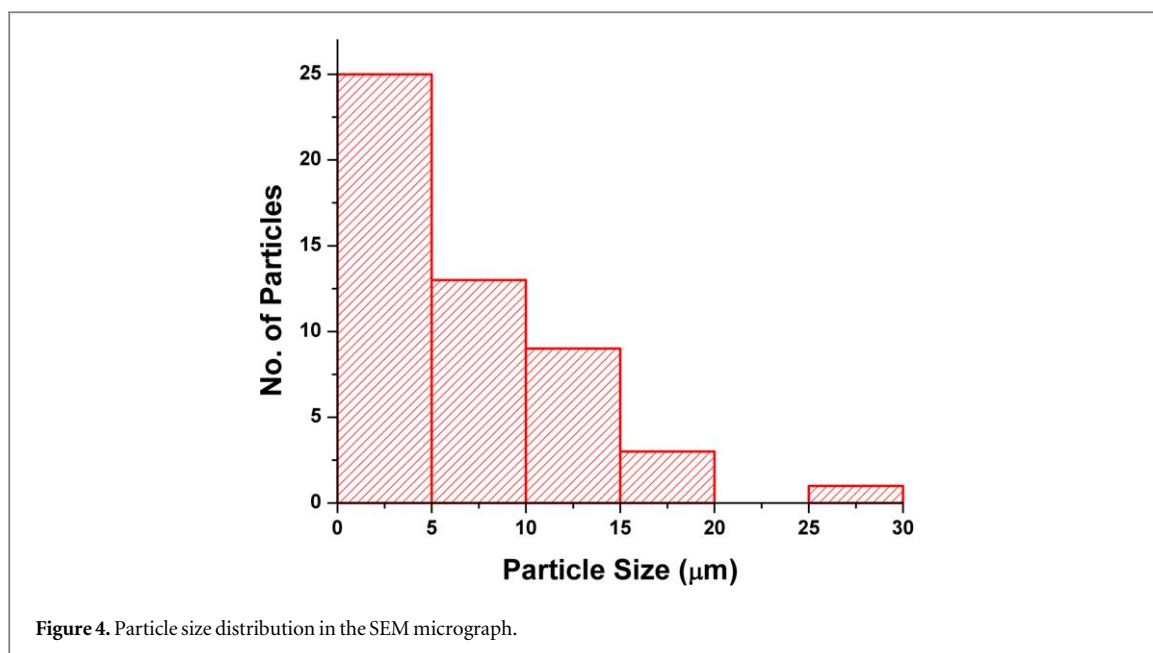


**Figure 3.** SEM micrographs of CoCrCuFeNi high entropy alloy powder milled at 65 h.

where  $L$  is the average crystallite size,  $\eta$  strain induced due to MA,  $k$  a constant (which in general is equal to 1.0). The Pseudo-Voigt method was followed for peak fitting and then the FWHM of the prominent peak was measured [35]. The decrease in crystallite size with increasing lattice strain concerning milling time is shown in figure 2. The morphology of the powder milled for 65 h has been studied through scanning electron microscopy (SEM) as given in figure 3. It could be observed that particles are flaky in nature and their sizes vary in the range of 2 to  $\sim 10 \mu\text{m}$  with a few exceptions of 15 to  $\sim 20 \mu\text{m}$  as shown in figure 4. This flaky nature of the particles is due to the heavy deformation involved during the mechanical working of the powder. The SEM EDX analysis of the 65 h milled powder is close to the nominal composition of the alloy as shown in figure 5 and suggests that the powder is homogeneous in composition.

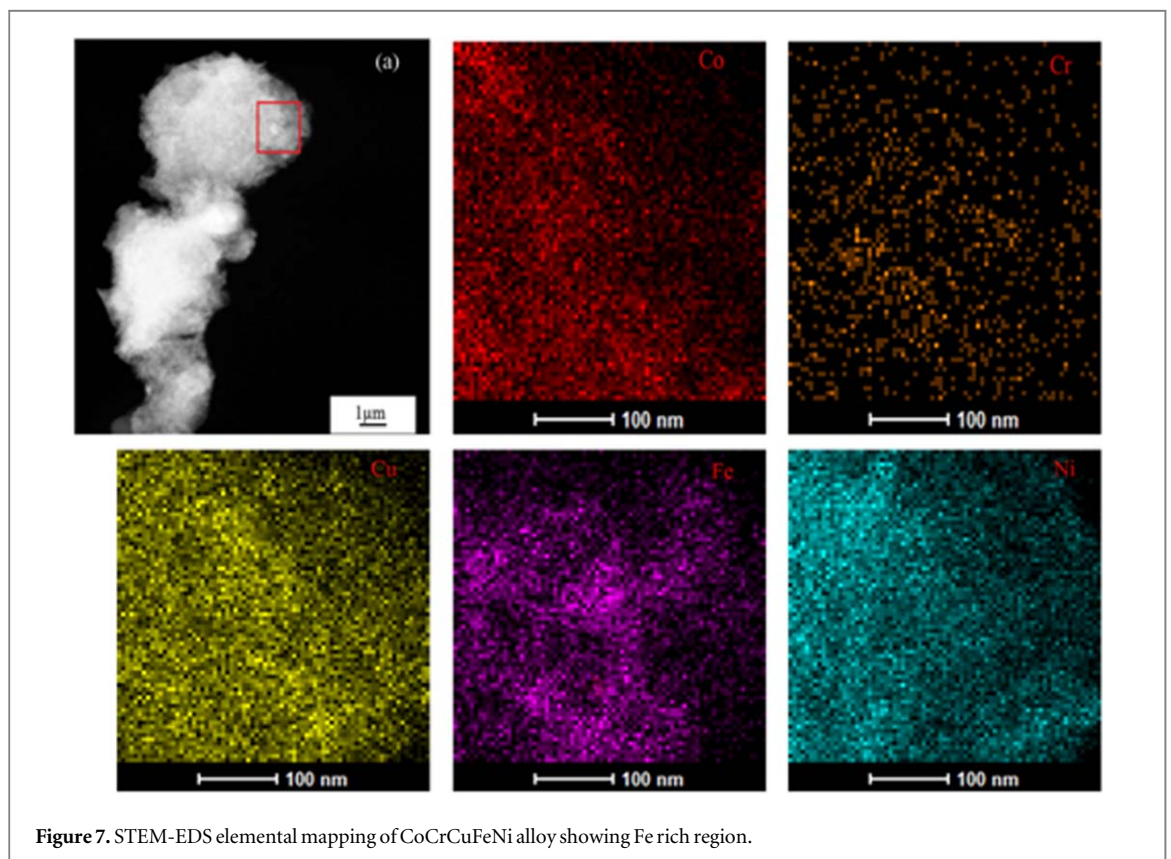
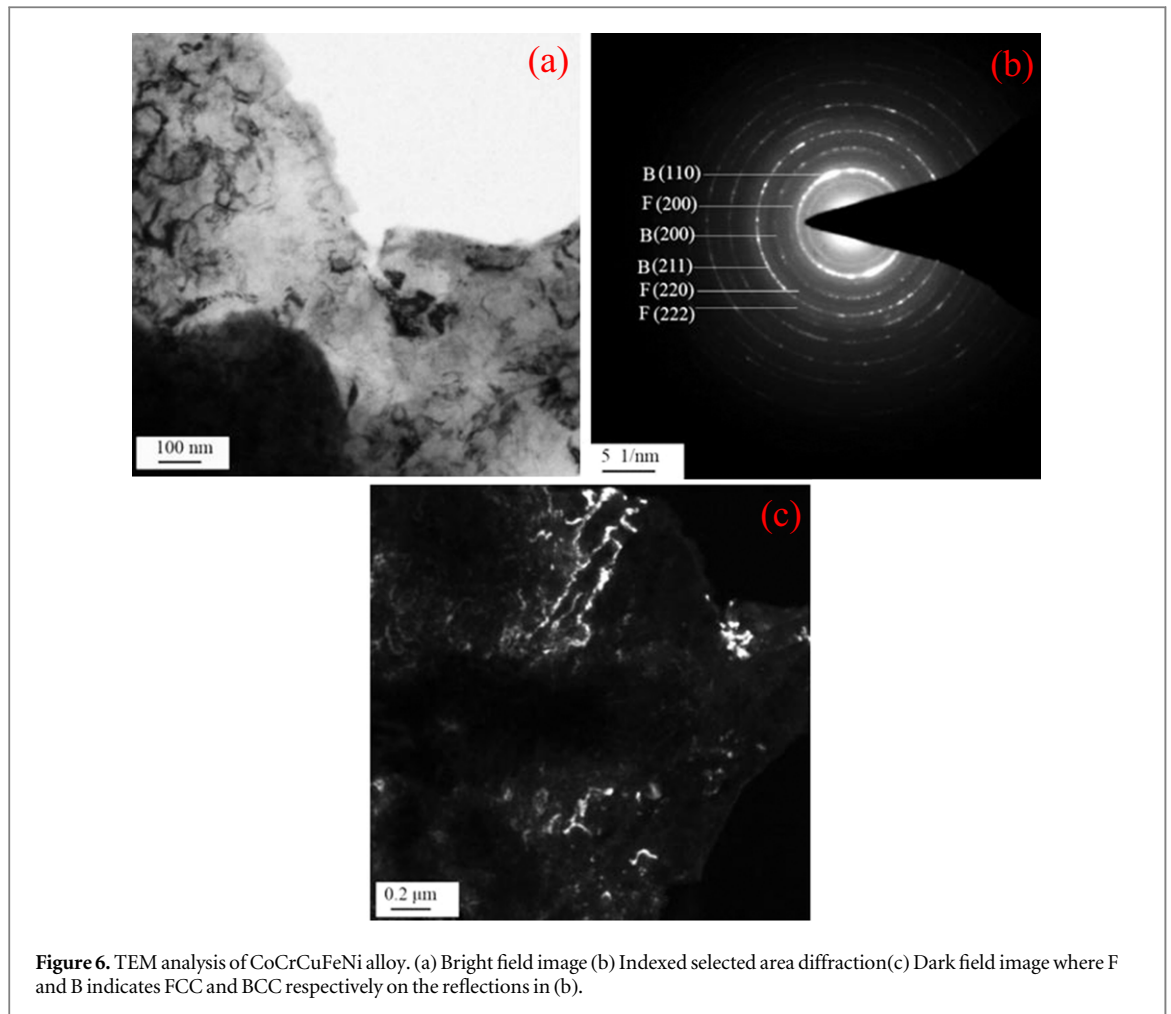
The existence of two phases can be seen on indexing the selected area diffraction (SAD) pattern obtained through transmission electron microscopy. The Bright field (BF), and corresponding selected area diffraction (SAD) pattern of the 65 h milled powder is given in figures 6(a) and (b). Indexing of the SAD pattern confirms the BCC solid solution phase ( $a = 0.285 \pm 0.002 \text{ nm}$ ). A diffuse ring of minor FCC ( $a = 0.360 \pm 0.002 \text{ nm}$ ) crystal. Figure 6(c) showed the center dark field image of the same area. It could be ascertained that a large fraction of the particles have sizes in the nanometer range. This is consistent with the fact that MA is well known for producing nanostructured materials. Formation of the uniform rings in SAD pattern indicates that the alloy particles are nanosized and randomly oriented in the alloy matrix. These results further corroborate the phase evolution by XRD analysis of the 65 h milled powder.

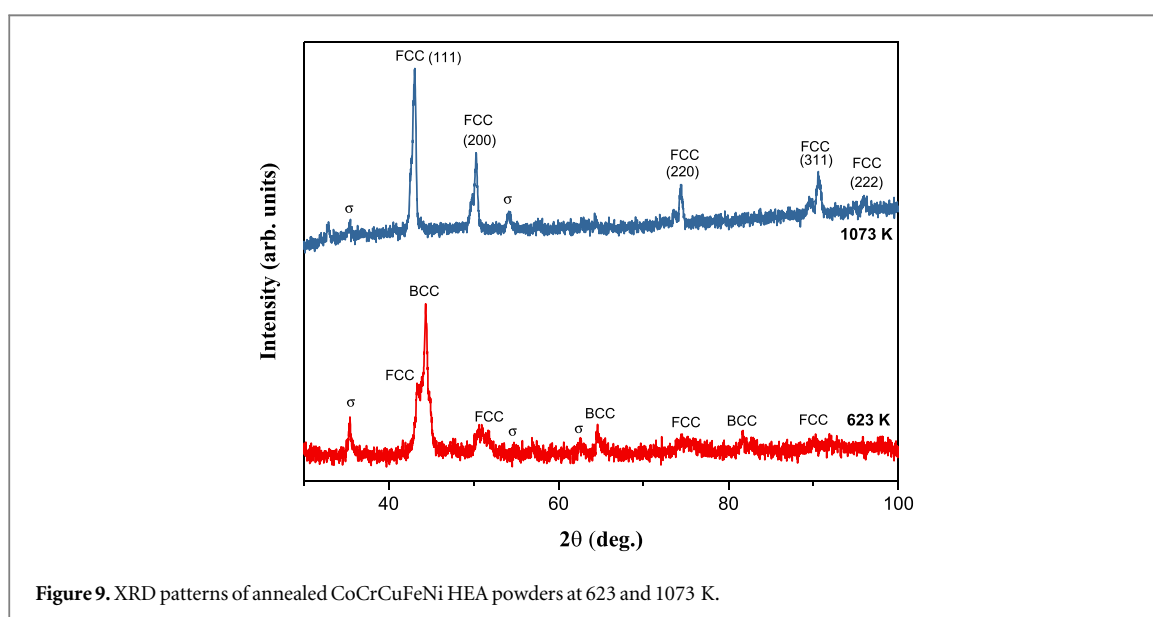
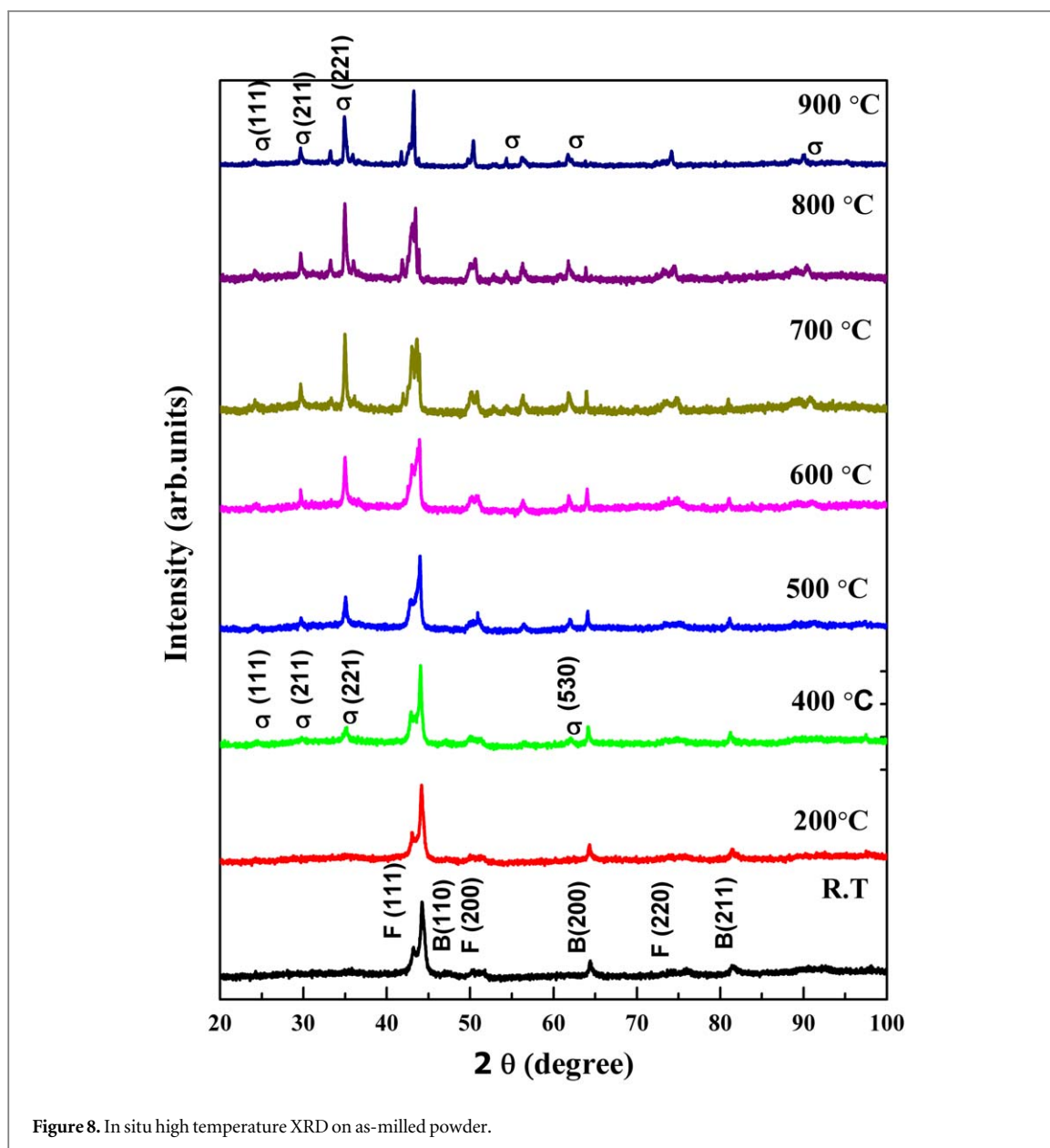
The STEM-EDS elemental mapping of 65 h milled powder is given in figure 7. It has been found from the elemental mapping that Fe, Cr, Co, Cu, and Ni are alloyed to form the BCC phase while some Cu remains unalloyed in the matrix as minor FCC phase.



### 3.3. Thermal stability of CoCrCuFeNi HEA

Diffusional transformations of phases in the chosen HEA, if any, is studied over a wide range of temperatures, the alloy was heated from room temperature to 1173 K in *in situ* heating XRD. The X-ray diffraction patterns corresponding to various temperatures are given in figure 8. At room temperature, similar diffraction peaks are observed as that of the milled powder after 65 h of milling. We can observe that the sample is stable below 673 K, above this new peaks become visible in the diffraction pattern ( $a = 0.845 \pm 0.002$  nm,  $c = 0.454 \pm 0.002$  nm) which closely matches with that of the ordered  $\sigma$  phase of Cr-Co/Fe. The peak intensity corresponding to (111), (211), (221) and (530) planes of  $\sigma$  phase increases as the sample is further heated through 873 K to 1173 K. The intensity of peaks corresponding to the minor FCC phase was found to be increasing with temperature, indicating that more FCC phase is forming. The intensities of (200) and (220) peaks corresponding to FCC phase start increasing above 673 K. It can be also seen that major peak (111) of FCC phase is slowly increasing with disappearance of the (110) peak of BCC phase. On the other hand (200) and (211) peaks of BCC phase show reduction in the intensity continuously with increasing temperature, and disappear at 1073 K. This implies that stable FCC phase is continuously evolving. This could be because the holding time in *in situ* heating XRD is not enough to complete the formation of the FCC phase due to slow diffusion. The powder sample was annealed at 1073 K for 2 h, analyzed by XRD (figure 9) in order to confirm the equilibrium phases present. A stable FCC phase ( $a = 0.362 \pm 0.002$  nm) got evolved along with a small amount of phase, while the BCC phase completely disappeared. The number of peaks and intensity of  $\sigma$  phase is more in *in situ* XRD compared to annealed sample at same temperature. This may be due to the small holding time in the *in situ* XRD compared to annealed sample. It may be predicted that the  $\sigma$  phase may also disappear completely with sufficiently prolonged annealing. The





CoCrCuFeNi alloys prepared by arc melting [23, 24] and Laser cladding [25, 26] have been shown to have FCC as a single stable phase. This shows that the FCC phase obtained after annealing of the 65 h milled powder at 1073 K for 2 h can be considered as a stable phase in this alloy.

On annealing the milled powder at 623 K, a small amount of sigma phase formation can be seen from figure 9. Thus, the onset temperature of the  $\sigma$  phase is approximately 623 K. The  $\sigma$  phase prone multicomponent system can be predicted through VEC values ( $6.88 \leq VEC \leq 7.84$ ) [36]. In the present context, VEC value is indicating for  $\sigma$ -free phase, but we are obtaining the  $\sigma$  phase on annealing above 673K. It is shown that the VEC range for the  $\sigma$  phase formation with that for the mixed FCC and BCC solid solutions formation:  $6.87 \leq VEC \leq 8$ . [28]. Hence VEC parameters are not valid for present alloys to predict  $\sigma$  phase formation. However, the formation of a two-phase mixture perhaps facilitates the formation of the  $\sigma$  phase.

## 4. Conclusions

Conclusions from the present work are as follows

- (i) The nanostructured CoCrCuFeNi equiatomic alloy prepared by MA is exhibiting two phases, one with BCC crystal structure having lattice parameter  $a = 0.287 \pm 0.002$  nm and a small amount of FCC phase having lattice parameter  $a = 0.362 \pm 0.002$  nm.
- (ii) The BCC and FCC phases formed by MA respectively are Fe-rich and Cu-rich as analyzed from STEM-EDS elemental mapping.
- (iii) The semi-empirical parameters calculated for the prediction of phases such as enthalpy of mixing and the weighted average of the atomic size difference is within the solid solution-forming range ( $-11.6$  kJ/mol  $< \Delta H_{mix} < 3.2$  kJ/mol and  $\delta \leq 6.6$ ).
- (iv) The synthesized HEA is stable up to 623 K and then due to diffusion assisted transformations  $\sigma$  phase precipitates.
- (v) A simple FCC phase ( $a = 0.362 \pm 0.002$  nm) is obtained after annealing the 65 h milled powder at 1073 K for 2 h, having a lattice parameter, which is very close to that of Cu ( $a = 0.361$  nm).
- (vi) The VEC ranges for predicting phase formation, are not valid in the present alloy. However, the formation of a two-phase mixture is predicted to facilitate the formation of the  $\sigma$  phase.

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