CHAPTER 5

AlCoCrFeNiTi HIGH-ENTROPY ALLOY

This chapter deals with the synthesis and characterization of equiatomic AlCoCrFeNiTi high-entropy alloy (HEA) processed by mechanical alloying (MA). Zhang et al. [104] have studied the similar alloy composition and reported the formation of a two-phase structure of BCC and FCC after MA. Transformation in the phase composition to two BCC solid solutions was observed after annealing at 600 °C for 1h. In their work of non-equiatomic $CoCrFeNiTiAl_x$ composition prepared by arc melting, the transformation of phase composition was observed from FCC to BCC on the addition of Al. To overcome all these inconsistencies, Ti was added as a sixth alloying element in AlCoCrFeNi alloy composition, in order to understand systematically the elemental dissolution with milling time, phase evolution, thermal stability and microstructural evolution. Phase evolution and thermal stability of the alloy was monitored by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and suitable heat treatments, respectively. The microstructural evolution of the microwave sintered alloy has been followed by scanning electron microscopy (SEM).

5.1 Phase formation

X-ray diffraction patterns of AlCoCrFeNiTi HEA milled powder with various milling time have been displayed in Fig. 5.1. Before milling (0 h), diffraction signals corresponding to all the constituent elements were observed. After 5 h of milling, it has been found that diffraction intensities of few peaks corresponding to Ti (d_{101}=2.228Å), Ti (d_{103} =1.32Å) and Ti, Al, Ni ($d_{112/311/220}$=1.23Å) start diminishing. Further, increase in milling up to 10 h, it has been noticed that the diffraction intensities of the low angle peak corresponding to Co start reducing earlier than other cubic structures. Earlier reports on mechanically alloyed high entropy alloys suggest that the melting point of the element is related to the disappearance of the peaks of the concerned elements [148].

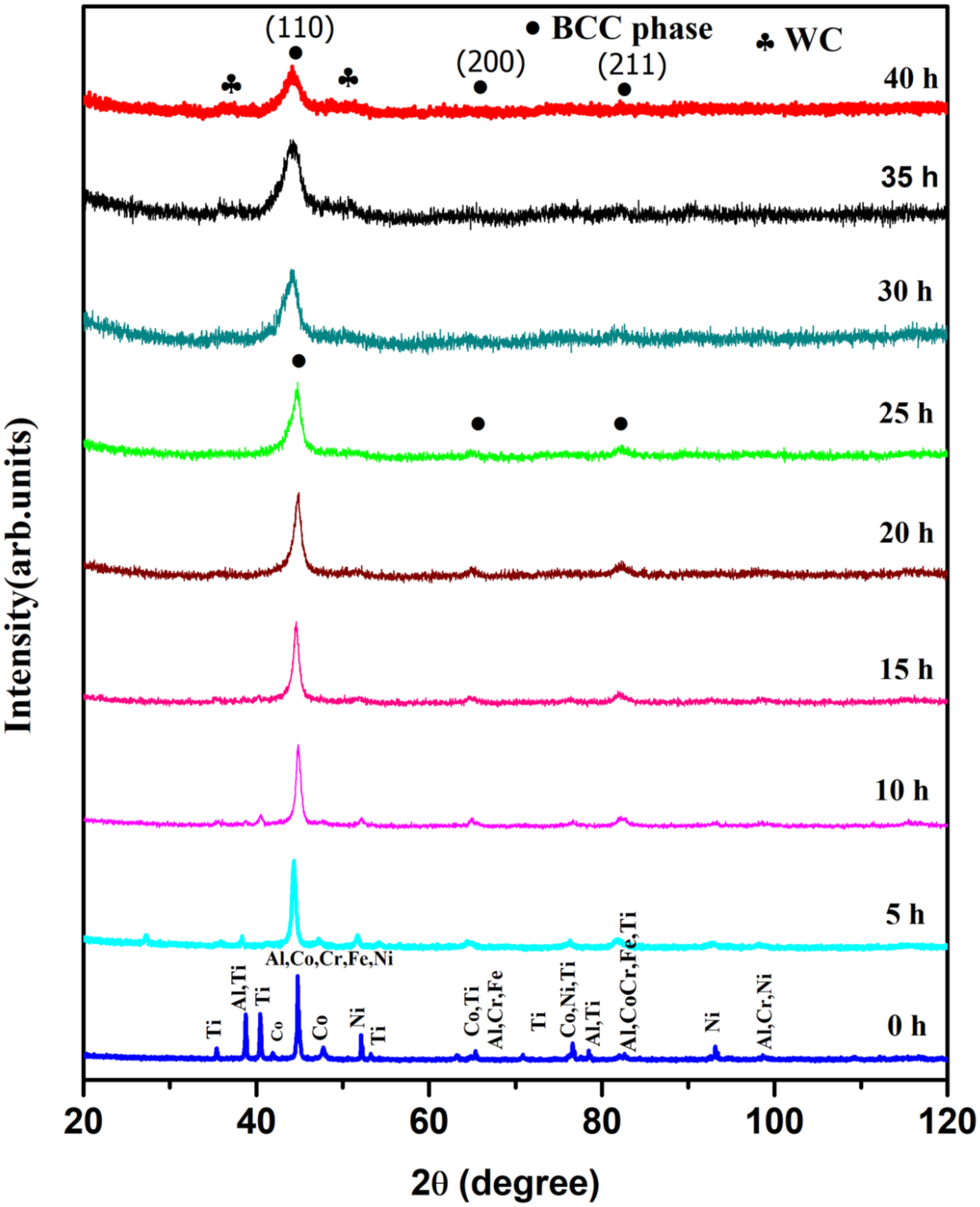

Figure 5.1: XRD patterns of AlCoCrFeNiTi HEA powders with different milling time. Evolution of BCC and WC phase was evident with the progress of milling.

Chen et al. [31] have reported that due to the lower melting temperature of the elements, it goes to the solid solution phase earlier than that of the high melting point elements due to faster diffusivity. Here it has been found that along with the melting point, the structure of the elements and the interaction with other elements also played an important role in forming the solid solution phase. Similar behaviour was observed in my previously reported AlCoCrFeNi and AlCoCrFeNiMn high-entropy alloy (chapter 3&4). However, it is also well established that alloying behaviour of elements during mechanical alloying is a function of many parameters. Further increase in milling for next 5 h gives more support to the above-mentioned statement. After 25 h of milling, peaks corresponding to the constituent elements disappeared, and the formation of a single-phase BCC structure was observed. In order to understand the alloying behaviour and phase stability of the alloy, milling was extended further. On increasing the milling time, it has been noticed that with the existing BCC (a = 2.85±0.01 Å) phase, new peaks corresponding to an unexpected phase appears. After careful investigation, it has been found that these signals conform to the existence of hexagonal tungsten carbide (WC) (a=2.90 Å, c= 2.83 Å) phase. This indication becomes more prominent on further increase in milling time up to 40 h. Throughout the diffraction patterns analysis, it has been noticed that the intensity of the major peaks decreases with increase in broadening. This behaviour was expected because the increase in milling time decreases the crystallite size and increases the lattice strain. It also supports the formation of nanocrystalline structure. Crystallite size and lattice strain were calculated by using the Williamson-Hall method with Xpert High Score plus software. The variation of crystallite size (nm) and lattice strain (%) with milling time of AlCoCrFeNiTi high entropy alloy has been reported in Table 5.1. It could be observed that at initial milling time, the decrease in crystallite size is prominent with significant induction of lattice strain. This increase in lattice strain is mainly due to the introduction of elements in the host lattice of the high-entropy alloy and mechanical working of powder during mechanical alloying processing [106, 149]. After 40 h of milling, it has been found that the diffraction intensities of the higher angle peaks are very weak in nature. This weak nature of the peaks (intensity) might be the reason for atomic mismatches (due to the constituent alloying elements), which destroyed the corresponding parent lattices.

Table 5.1: The calculated values of the crystallite size (nm) and lattice strain (%) in AlCoCrFeNiTi high-entropy alloy at different milling schedules.

Milling time (h)	**AlCoCrFeNiTi**	
	Crystallite size (nm)	**Lattice strain (%)**
5	36	0.33
10	30	0.38
15	13	0.82
20	11	1.02
25	11	1.03
30	10	1.21
35	10	1.22
40	10	1.23

5.2 Analysis of powder morphology

The morphology and size of the powder particles were investigated using scanning electron microscopy (SEM). Fig. 5.2 (a&b) shows the secondary electron micrographs of 40 h milled AlCoCrFeNiTi HEA powder. It is observed that nanosize particles got agglomerated and formed micron size particles. These micron range particles are varying in the range of 3 to 18 microns. This is happening, because during mechanical alloying, powder particles get flattened, cold-welded and fractured repeatedly. The process of welding and fracturing reaches a saturation value after a certain period.

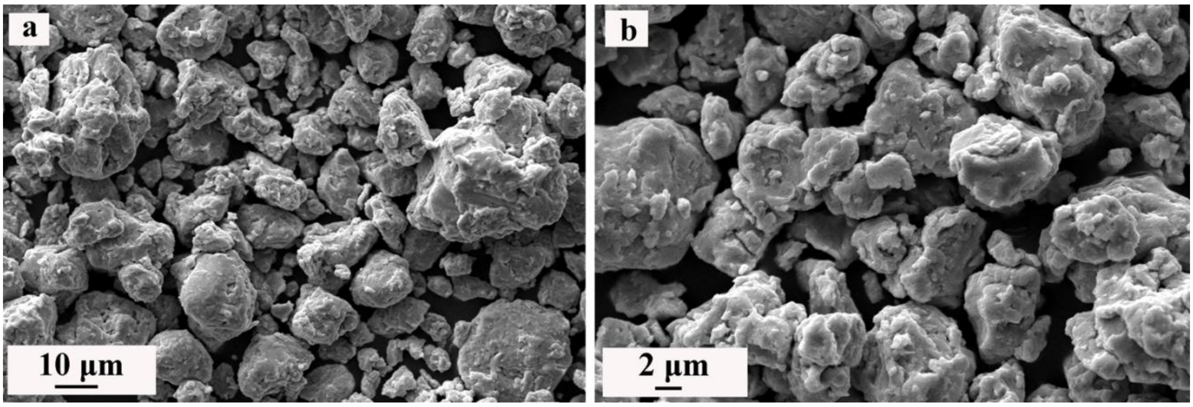

Figure 5.2: SEM micrographs of AlCoCrFeNiTi HEA powders with 40h of milling at different magnifications (a&b). In both cases, fractured particles with agglomerated form can be observed.

5.3 Nanostructured nature and phase confirmation

Phase evolution and alloying effects have also been confirmed through transmission electron microscopy (TEM). Bright field, corresponding SAD and dark field image has been shown in Fig. 5.3. In the bright field image, highly strained regions can be seen. Formation of diffuse ring patterns in the SAD confirms that the particles are strained and randomly oriented. Indexing of the ring pattern further corroborates the formation of the BCC phase along with tungsten carbide (WC). The dark filed imaging on the BCC reflections shows that the phase is in the nanometer ranges, confirming the evolution of nano BCC phase. High-resolution imaging of the 40 h milled powder sample has been shown in Fig. 5.4. It has been ascertained that similar ‘d’ spacings of the BCC phase were observed in Fig. 5.4 (a). From indexing of the lattice fringes in Fig. 5.4 (b) it can be confirmed that some intermetallic phase has been formed after mechanical alloying. Careful investigation realizes that few fringes are corresponding to the WC phase.

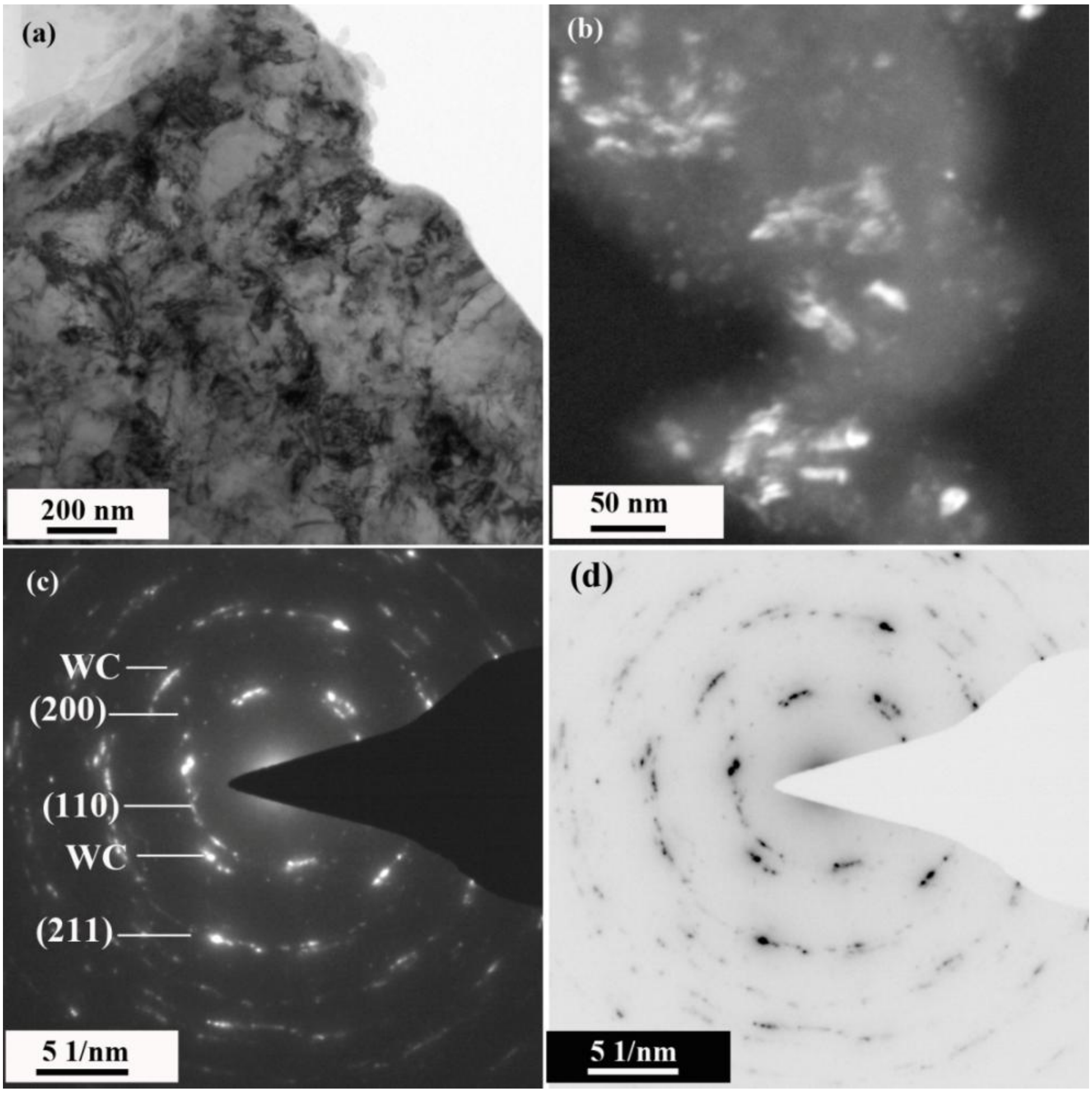

Figure 5.3: TEM images of 40h milled AlCoCrFeNiTi high-entropy alloy powder. (a) Bright-field image (b) dark-field image, (c) SAD pattern, (d) inverted SAD pattern for better visibility. Indexing of ring pattern confirmed the formation of a solid solution phase of BCC crystal structure along with the WC phase.

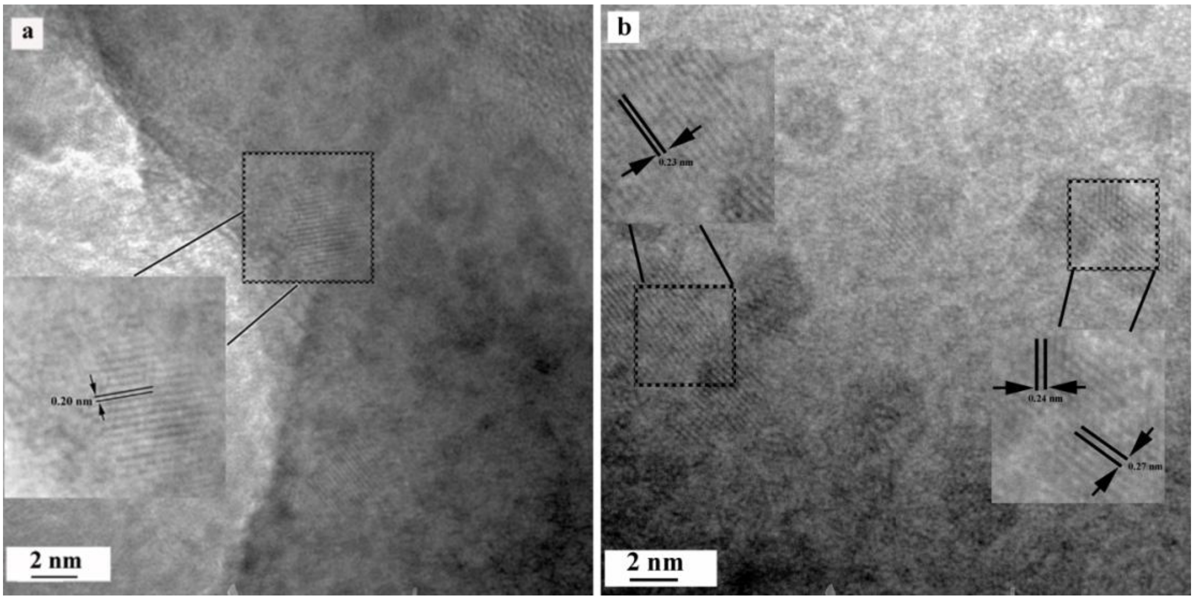

Figure 5.4: High-resolution imaging of the 40 h milled AlCoCrFeNiTi high entropy alloy powder. (a) Lattice fringes of similar 'd' spacing of BCC phase were observed. Formation of the WC phase was also observed (b).

The chemical compositions of the constituent elements were analyzed using HAADF, and STEM-EDS mapping of the 40 h milled AlCoCrFeNiTi high-entropy alloy, which is displayed in Fig. 5.5. It could be visualized that all the constituent elements are homogeneously distributed in the matrix of the AlCoCrFeNiTi high entropy alloy. It confirms that all the constituent elements are present homogeneously, leading to high entropy of the alloy. Moreover, in the STEM-EDS mapping, uniform distribution of WC phase could not be observed. This confirms that the WC phase is present locally and it cannot be treated as the character of the high entropy alloy.

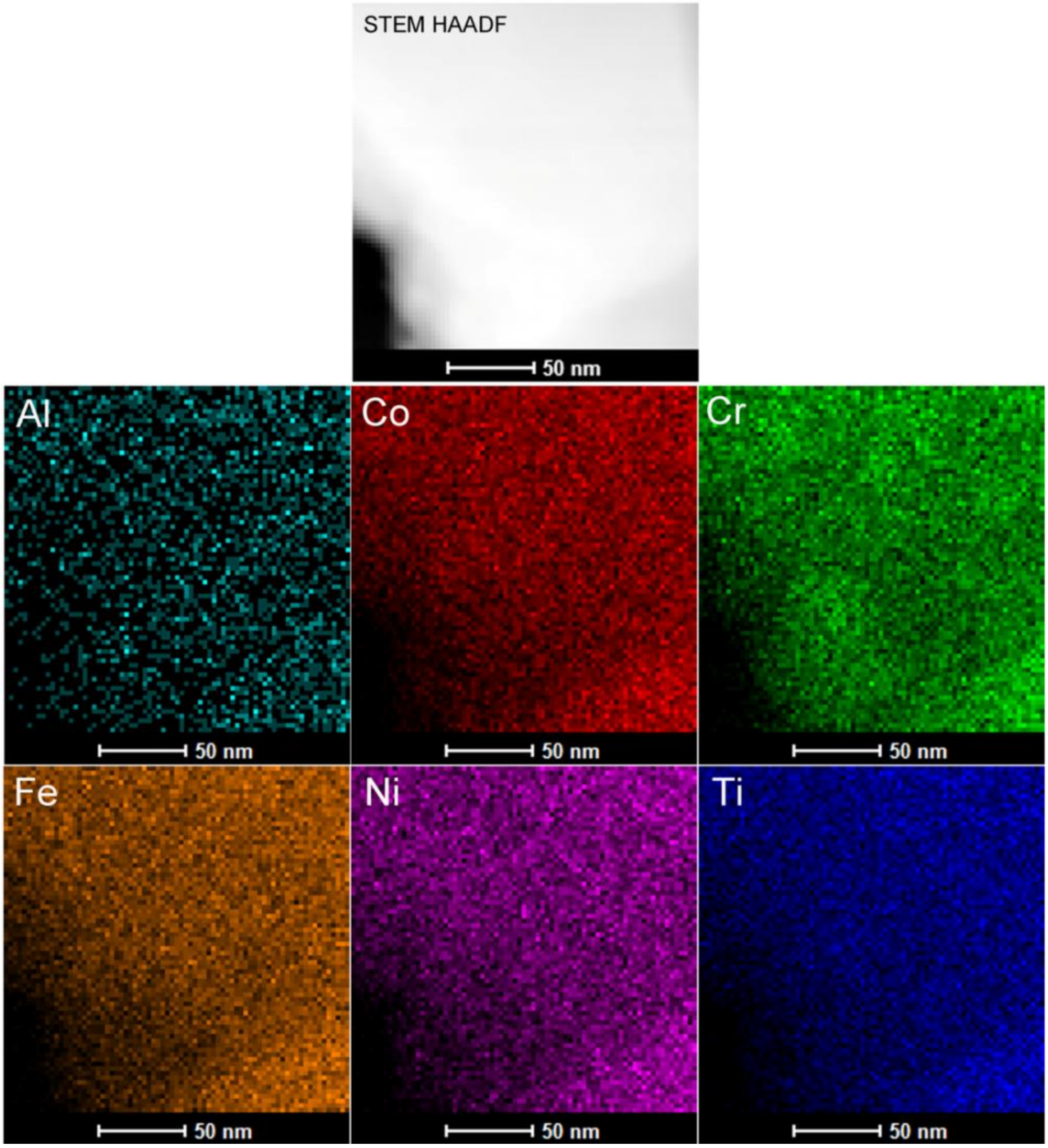

Figure 5.5: The STEM-EDS mapping of equiatomic AlCoCrFeNiTi hexanary high entropy alloy after 40h of milling. No segregation of elemental composition was observed.

5.4 Thermal stability

The DSC thermograms of the 40 h milled AlCoCrFeNiTi high entropy alloy has been shown in Fig. 5.6. This thermogram is the plot of the energy evolved during the heating the alloy powder up to 1200 ºC (1473 K) with three heating rates i.e. 20, 40 and

50 K/min respectively. It has been found that there was no sign of phase change at 20 and 40 K/min heating rates. Further increase in the heating rate (50 K/min) showed the presence of two thermodynamic heat events. First heat event that is exothermic in nature shows their signal at around 360 ºC (633 K) and second event which is associated with the endothermic at around 655 ºC (928 K). The first exothermic event is related to the release of internal stresses, such as structural deformation and lattice strain [150, 151]. The second peak (endothermic in nature) at around 928 K in the DSC thermogram might be the precipitation of the B2 phase.

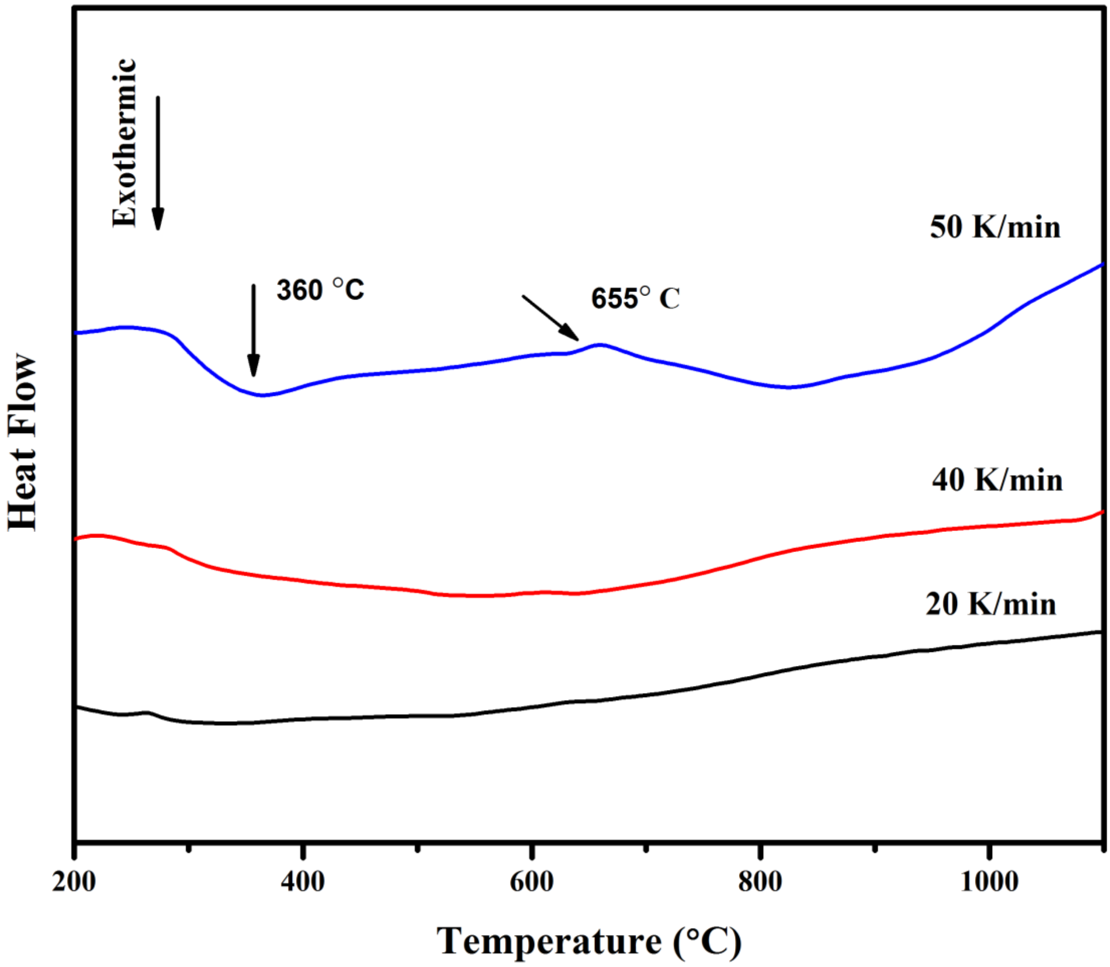

Figure 5.6: DSC thermogram of 40 h milled nanocrystalline equiatomic AlCoCrFeNiTi HEA heated to 1200ºC. First heat event is related to the release of the internal stresses, and the second might be related to the speculation of the B2 phase.

In DSC thermograms, it has been observed that no peak (in 50 K/min heating rate) shows the sharp nature during the heat evolution. It can be elucidated that in high entropy alloys due to the presence of the several elements in the alloy matrix, the kinetics of the phase change is very slow in nature and time-dependent. Therefore, the phase transformations in all these alloys are diffusional in nature and depend on the range of temperature and time. Fig. 5.7 shows the in situ high-temperature XRD plots of the 40 h milled AlCoCrFeNiTi HEA powder. These temperatures were selected based on heat events evolved in the DSC thermogram. It has been noticed that the first heat event in DSC thermogram was around 360 ºC (633 K) which might be related to the release of the internal stress. There was no change in phase constituents after heat treatment at this temperature (633K). Further selected temperature (600 ºC) also falls in the same line and confirmed that there is no transformation. Therefore, from this study, it can be concluded that AlCoCrFeNiTi alloy is stable up to 600 ºC (873K).

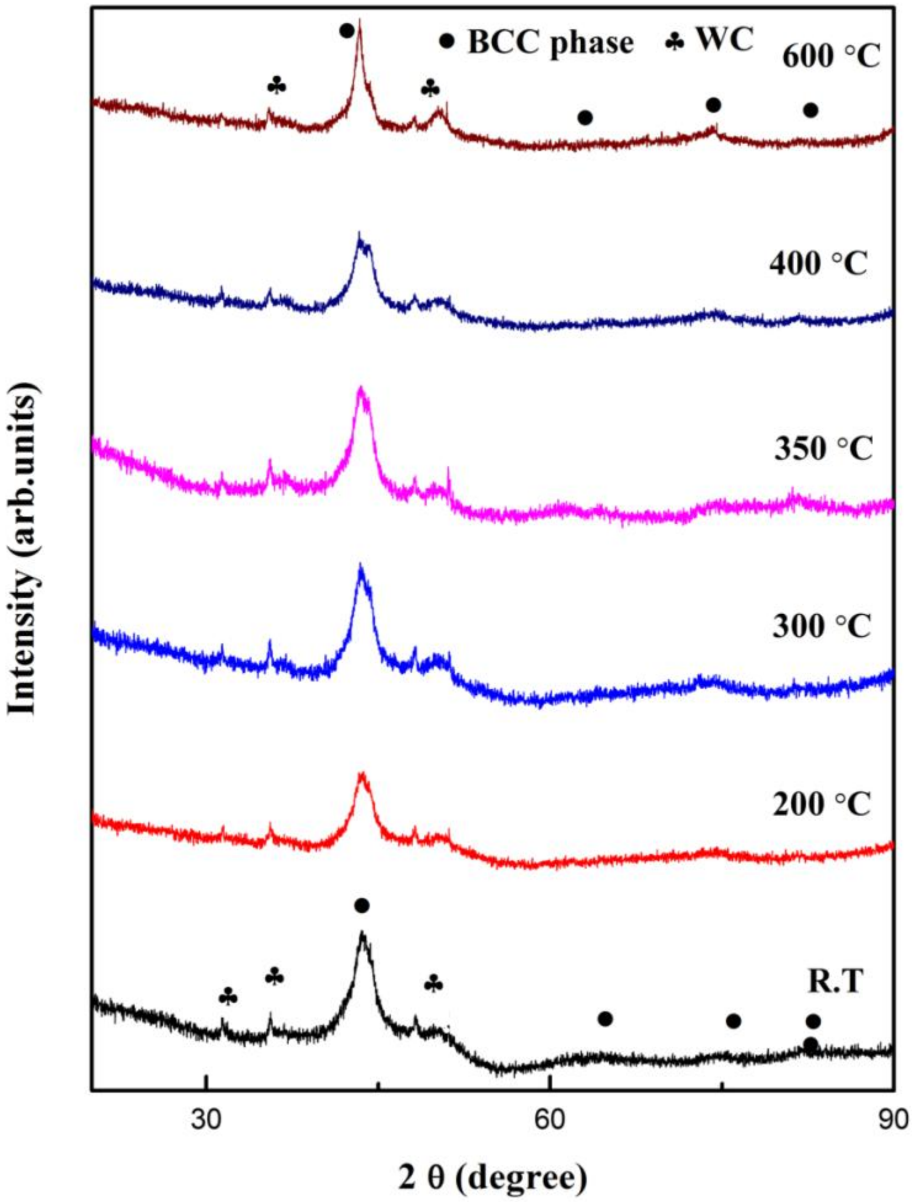

Figure 5.7: In-situ XRD patterns of 40h milled AlCoCrFeNiTi high entropy alloy powder upto 600 ºC (873K). No phase transformation is observed, which signifies that the alloy is stable upto 600 ºC (873K).

5.5 Microstructure and phase evolution in sintered alloy

The secondary electron imaging of the microwave sintered pellet has been given in Fig. 5.8 at different magnifications. Two types of the particle could be visualized from electron micrographs. It has been found that particles of sizes in the range of 7 to 12 micron are formed after microwave sintering.

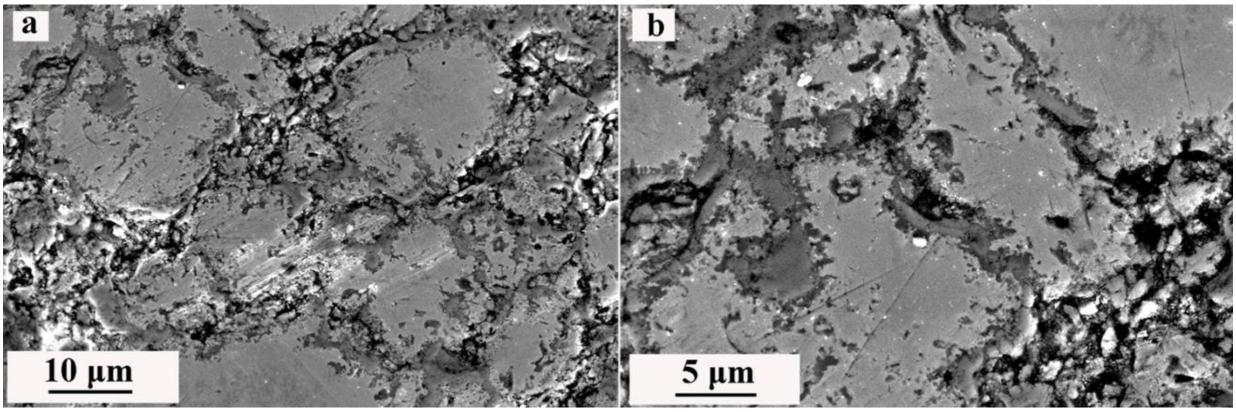

Figure 5.8: Secondary electron imaging of the microwave sintered pellet at 1000ºC of AlCoCrFeNiTi high entropy alloy at two different magnifications.

Some amount of porosity could also be observed from the SEM micrographs. Therefore, from this study, it could be concluded that density and porosity is the major concern in the microwave-sintered samples. High density with better homogeneity can be achieved through powder metallurgy route if pressure is applied during the sintering, likewise SPS and hot pressing. XRD pattern of microwave sintered AlCoCrFeNiTi high entropy alloy compacted at 1000 ºC (1273 K) has been illustrated in Fig. 5.9.

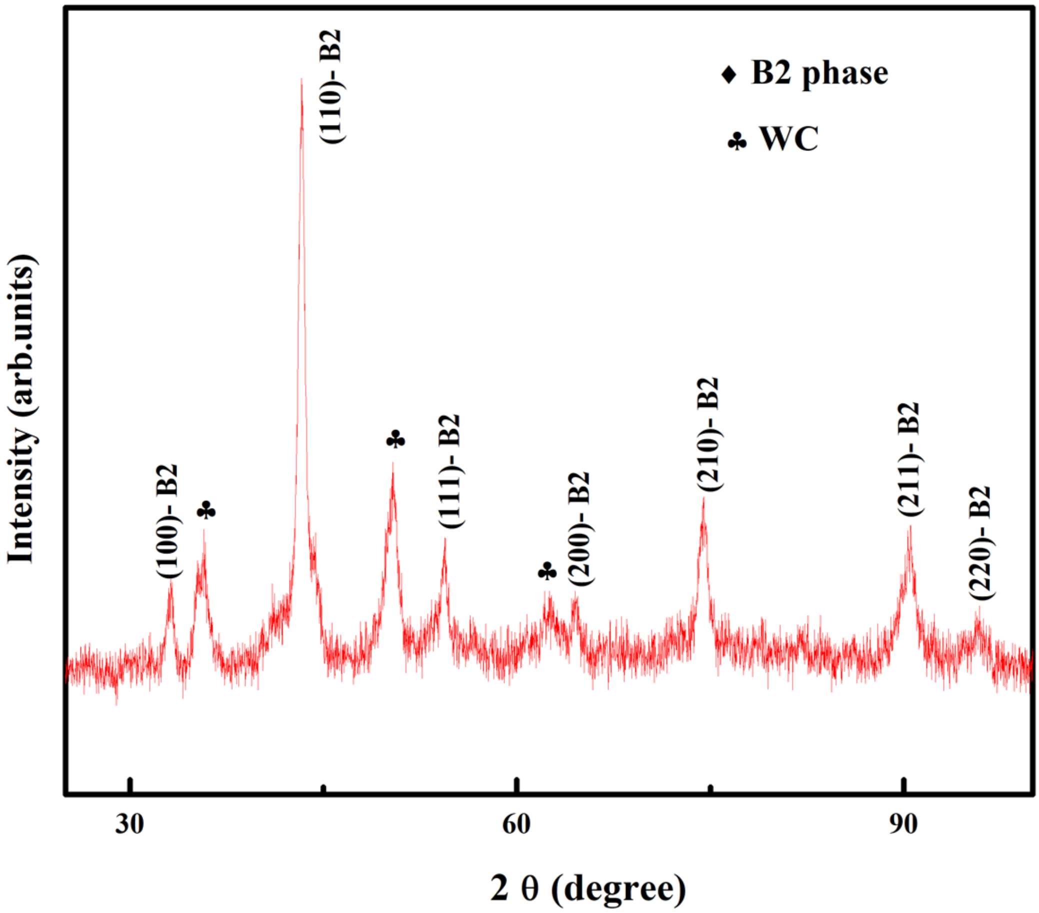

Figure 5.9: XRD patterns of AlCoCrFeNiTi alloy compact after microwave sintering at 1000 ºC (1273K). The evolution of B2 type phase along with the formation of WC phase can be discerned.

It has been found that after microwave sintering, BCC phase transforms into the B2 (a= 2.87±0.03Å) type phase along with the hexagonal phase. The increase in diffraction intensity results from the coarsening of the crystal and release of the internal stresses.

5.6 Discussion

5.6.1 Solid solution forming criteria

High-entropy alloys are getting more attention over more than a decade due to their simple solid solution phase forming ability. An important question related to the design of these multi principal alloys is not clearly understood. It has been reported that these alloys are forming the simple solid solution phases due to high mixing entropy (ΔS_{mix}). This high mixing entropy lowers the Gibbs free energy (ΔG_{mix}), which promotes the different elements to be randomly distributed in the crystal lattice. This reduces the tendency of ordering and segregation in the alloy. In addition to that, thermodynamically, it has been found that the effect of high mixing entropy (ΔS_{mix}) becomes more prominent as the temperature increases. Zhang et al. [34] have proposed phase forming criteria in HEAs using parameters such as enthalpy of mixing (ΔH_{mix}) and delta parameter (δ) to form a simple solid solution phase. In the same approach, Yang et al. [35] have suggested that solid solutions with a simple crystal structure is formed when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ (equations in chapter 1). The enthalpy of mixing (ΔH_{mix}) for multicomponent alloy system was calculated from the Miedema's macroscopic model for binary alloys [38]. The calculated results of all these parameters are reported in Table 5.2.

Table 5.2: Calculated thermodynamic parameters for AlCoCrFeNiTi high entropy alloy.

ΔH_{mix} (kJ/mol)	**T_m (K)**	**ΔS_{conf} (J/mol-K)**	**δ (%)**	**Ω**
-21.56	1720	14.89	6.58	1.19

The Ω of this alloy system is ~ 1.19, which is in good agreement to form solid solution phase ($\Omega > 1$). Along with Ω factor delta factor (δ) is also in range for the AlCoCrFeNiTi HEA to form a solid solution. These two factors are implying that simple solid solution phase can be formed theoretically and getting validation from experimental results.

5.6.2 Alloying behaviour

Alloying behaviour and the phase evolutions in the AlCoCrFeNiTi HEA were monitored at a specific time schedule shown in Fig. 5.1. It has been found that Ti, Co and Al are the elements, which go to the lattices of the solid solution first compared to the other constituents of the alloying elements. It could be concluded that apart from the melting point structure of the constituent elements is also an important factor. Throughout the milling process, peak intensity decreases with an increase in broadening due to mainly reduced crystal sizes, the evolution of high lattice strain and a decrease in crystallinity (Table 5.1). A single-phase solid solution of BCC phase was observed after 25 h of milling; milling was extended up to 40 h of milling in order to understand the possibility of further change in phases. It has been found that some extra peaks appeared as the milling continued. Careful investigation suggests that these peaks are corresponding to the tungsten carbide (WC). It helps in understanding that milling powder has been contaminated during prolong milling. Noticeably it is happening after a definite time period. The formation of carbide has arisen due to the wet atmosphere of milling using toluene for mechno-chemical reaction. Here toluene reacted with the WC vials & balls and led to the formation of the carbide phase. From this study, it can be concluded that high energy ball milling in a wet atmosphere after a certain period of time started contaminating the powder. However, it may be emphasized that the formation of WC does not change the composition of high entropy alloys formed as the content of all these six elements does not get affected. The presence of these phases has been ascertained through transmission electron microscopy. From the mixing enthalpies of the binary atomic pairs in Table 5.3 of AlCoCrFeNiTi high-entropy alloy, it shows that this alloy is possesses limited solid solubility under an equilibrium condition.

Table 5.3: The chemical mixing enthalpy (ΔH_{mix} (kJ/mol)) of atomic pairs of AlCoCrFeNiTi high entropy alloy calculated by Miedema approach.

Element	Al	Co	Cr	Fe	Ni	Ti
Al	-	-19	-10	-11	-22	-30
Co	-19	-	- 4	-1	0	-5
Cr	- 10	- 4	-	-1	-7	2
Fe	- 11	- 1	- 1	-	-2	0
Ni	- 22	0	- 7	- 2	-	- 52
Ti	-19	- 42	-11	- 25	- 52	-

Here, the solid -solubility extension is mainly governed by high mixing entropy (in HEAs) and non-equilibrium state of the mechanical alloying process. This high mixing entropy of alloy lowers the tendency to form the intermetallic and ordered phases and supports to form stable solid solution phases. It can be concluded that the formation of simple solid solution phases after mechanical alloying is dependent on composition and processing routes.

5.6.3 Thermal stability

From the differential scanning calorimetry thermogram, it has been found that there were two separate heat events evolved when the powder is heated up to 1200 ºC (1473 K). First heat event is exothermic in nature around 360 ºC (633 K) and related to the release of the internal stresses induced during the mechanical working of the alloy. Second heat event is endothermic in nature at around 650 ºC (923 K) which might be the speculation of the phase transformation. To ascertain these two events, in-situ high-temperature XRD was done at the selective temperatures. It is observed that this alloy is stable up to 600 ºC (873 K) because there was no phase change found in the XRD plot. Similar kinds of phases observed were present in the 40 h milled powder alloy. Microwave sintered AlCoCrFeNiTi high entropy alloy at 1000 ºC (1273 K) showed that the BCC phase transformed to ordered B2 (a= 2.87±0.03Å) type phase. It has been reported in the literature that the formation of intermetallics are somehow empirically related to the heat of mixing [143]. For current alloy, the heat of mixing is higher for the Ni-Ti and Al-Ni among all the other alloying elements. Therefore, the formation of intermetallic phases in the AlCoCrFeNiTi HEA can be justified through their heat of mixing.

5.7 Conclusions

The following conclusions can be drawn from this chapter-

1. The equiatomic composition of AlCoCrFeNiTi (hexanary) high-entropy alloy leads to the formation of a single-phase BCC structure (a= 2.85±0.01Å) with minor WC phase after 40 h of mechanical alloying. The evolution of WC phase (hexagonal, a=2.90Å, c=2.83Å) is due to the contamination of the milling media and process controlling agent.
2. Phase stability of the AlCoCrFeNiTi has been confirmed through differential scanning calorimetry and in-situ high-temperature XRD and found that this alloy is stable up to ~600 ºC (873K).
3. The semi-empirical thermodynamic analysis reveals that the ratio of $T\Delta S/\Delta H$ (Ω) is ~1.19, which is well within the range of the solid solution phase forming criterion of high entropy alloy.
4. Consolidated and sintered pellets of AlCoCrFeNiTi HEA shows the evolution of a B2 type phase (a=2.87±0.03Å) along with minor WC phase arising from the milling media.