

Determination of microstructural properties and its effects on hardness of FeNiCrCoAl_x (x=0,20 at%) high entropy alloys

By

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Abstract

In recent years, the concept of high entropy alloys (HEAs) has gained increasing attention due to their unique compositions, microstructures and properties. High entropy alloys are defined as solid-solution alloys with 5 or more principal elements in equal or nearly equal atomic fractions with the elemental concentrations ranging from 5 – 35at%. This new class of materials are considered to be potential alternatives to the conventional materials which are currently being used in the different fields such as structural, nuclear, automotive and aerospace industries.

In this study, the determination of phases and microstructural properties of FeNiCrCo and FeNiCrCoAl high entropy alloys with nearly equi-atomic concentrations and their influence on the hardness of the material after undergoing different thermo-mechanical treatments was studied. The combination of different techniques such as, X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS) and Electron backscattered diffraction (EBSD) were used to determine the phases present in the alloy systems for different experimental conditions. Optical microscopy, scanning electron microscope (SEM) were used to observe the microstructural evolution in the material. Vickers hardness tester is used to determine the hardness values.

FeNiCrCo high entropy alloy system was found out to be a single-phase FCC system for all experimental conditions whereas FeNiCrCoAl contains a mixture of BCC, FCC and Sigma phases. The hardness values were correlated to the phases present and the microstructural properties of the alloy. This study provides an overview of the behavior of these alloy systems from intermediate to high temperature range for two different starting conditions, as cast and hot rolled. This work can be considered as a first step to fully understanding the potential of these high entropy alloy systems to serve as potential alternatives to the conventional alloys currently used.

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1. Introduction

From the beginning of bronze age, alloy design follows the development of a system with one or two principal elements whose properties are altered to achieve desired properties by minor additions of other elements. Some of the examples of these alloy systems are Fe-based systems (steels), Ni-, Al-, Ti- Cu-, based alloys.

By 1970s, majority of the high-performance alloys currently being used had been developed, which is regarded by many as the period when traditional alloys had reached their maturity.[1] Since this time, various routes have been taken to meet the continuous demand for materials with enhanced properties for advanced applications. One approach has been to employ novel production routes, such as thermo-mechanical treatments, rapid solidification, mechanical alloying, spray forming, superplastic forming, stir friction welding, nanoscale material production. Another method has been to manipulate the composition of the alloys, as in the case of newly developed intermetallic compounds and their alloys, metal matrix composites, Al-Li alloys, metallic glasses, lead-free solders, and nanostructured materials. There has also been a lot of work which combines both processing and compositional routes for the further development of materials.[2]

In an attempt, to overcome the diminishing returns in satisfying many of the above criteria from conventional alloy systems, which are typically based on one or, at most, two major elements, J.W.Yeh[1], in 1995, started to explore multi-principal-element alloys termed as “high-entropy alloys” (HEAs), which emphasizes their inherent high mixing entropies.[2][3]

High entropy alloys are defined as a solid-solution alloys containing 5 or more principal elements (up to 13 elements) in equal or nearly equal atomic fractions. The concentration of each principal element ranges from 5 to 35 at%. These alloy systems exist in the centre of the phase diagram whereas the conventional alloys reside at the edges of the phase diagram as shown in Figure 1.[2][3][4]

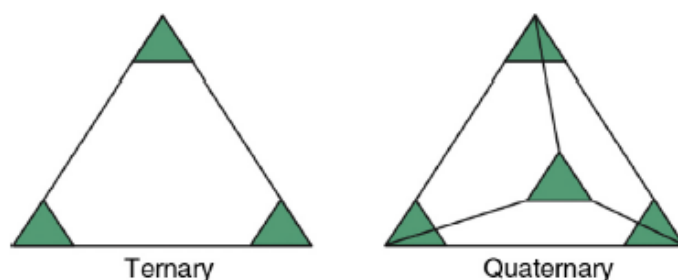


Figure 1 Schematic ternary and quaternary alloy systems, showing regions of the phase diagram that are relatively well known (green) near the corners and relatively less well known (white) near the centre[3][4]

Initially these new multi-principal-element alloys seemed very complex in composition and microstructure, and difficult to analyse, which was aggravated by the lack of literature. However, after a period of research, it was discovered that the synthesis, processing, and analysis of these alloys was practical. This opened the door to a whole new world of alloy design with great potential in both academic study and commercial applications.[2]

Cantor [5] also pointed out that a conventional alloy development strategy leads to an enormous amount of knowledge about alloys based on one or two components, but little or no knowledge about alloys containing several main components in near-equal proportions which he referred to as multi-component alloys. These alloy systems are also called by other names such as equi-molar alloys, equi-atomic ratio alloys and substitutional alloys.[3][4]

1.1. Area of focus

High entropy alloys is a new approach in the development of materials for advanced applications where properties such as corrosion resistance, mechanical properties at high temperatures as well as for cryogenic temperatures and oxidation resistance are crucial. These new alloys are to be extensively studied, to understand and fully utilize their unique and attractive properties in the present-day applications.

The combinations of the high entropy alloy systems studied in this report are selected from the literature. The high entropy alloy of the combination FeNiCrCo is considered as one of the base alloys for the high entropy alloy systems. Other elements like Al, Mn, Ti are added to achieve desired properties and are extensively studied alloy systems. Table 1 contains the combination of high entropy alloy systems that are focused in this report.

Table 1 Composition distribution of the high entropy alloys studied. All quantities mentioned are in weight%

Sample	Fe	Ni	Cr	Co	Al
FeNiCrCo	24.76	26.04	23.07	26.13	
FeNiCrCoAl	22.11	23.26	20.60	23.34	10.70

In this report, we focus on the study of the influence of grain size and phases present on the hardness of the material after undergoing different thermo-mechanical treatments.

In chapter 2, we discuss the underlying principles which govern high entropy alloy and properties of the high entropy alloy systems studied from the literature. In chapter 3, the experimental details and characterization techniques used are explained. Further in chapter 4, we focus on the results and discuss the obtained results in detail.

2. Literature review

2.1. Thermodynamics and Design principle of High entropy alloys

Thermodynamically, a system tries to minimize its Gibbs free energy (G), in other words, equilibrium is reached when the G value reaches minimum. The Gibbs free energy of an elemental system can be calculated by the following equation,

$$G = H - TS \quad (1)$$

where, H represents the enthalpy, S represents entropy and T represents temperature. It is observed that the enthalpy and entropy at a given temperature determines the free energy value and the equilibrium state of the elemental system. For the prediction of equilibrium state of an alloy, the Gibbs free energy changes from the elemental state to other states are compared to determine the state that results in the lowest Gibbs free energy of mixing (ΔG_{mix}). From equation (1), the relation between differences in Gibbs free energy (ΔG_{mix}), enthalpy (ΔH_{mix}) and entropy (ΔS_{mix}) between the elemental and mixed states is,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (2)$$

From the Boltzmann's hypothesis, the entropy of mixing for a N -element alloy system changing from elemental state to a random solution state can be calculated using the formula,[4][6]

$$\Delta S_{mix} = -R \sum_{i=1}^N C_i \ln C_i \quad (3)$$

where, C_i is the atomic percentage of the i th component and R is the gas constant (8.31 J/K mol).

The value of mixing entropy calculated from equation (3) reaches the maximum for an equi-atomic alloy system and can be calculated using equation (4) [4][6]

$$\Delta S_{mix} = R \ln (N) \quad (4)$$

From equation (4), the configurational entropy value increases as the number of elements in the equi-atomic alloy system increases as depicted in Figure 2.[2]Figure 2 The entropy of mixing as a function of the number of elements for equimolar alloys in completely disordered states

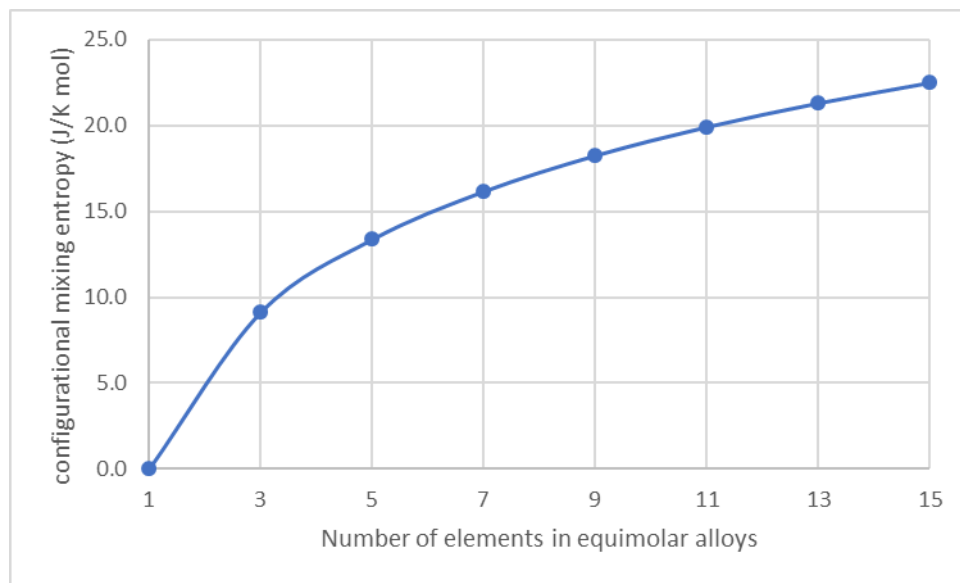


Figure 2 The entropy of mixing as a function of the number of elements for equimolar alloys in completely disordered states[2]

From equation (2), the other factor that influences Gibbs free energy is enthalpy of mixing (ΔH_{mix}). Based on the regular melt model, the enthalpy of mixing can be determined as [4][6]

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n \Omega_{ij} C_i C_j \quad (5)$$

where, Ω_{ij} ($= 4 \Delta H_{AB}^{mix}$) is the regular melt interaction parameter between the i th and j th elements and ΔH_{AB}^{mix} is the mixing enthalpy of binary liquid alloys and C is the atomic percentage of i th and j th elements.

According to Hume-Rothery, the important factors that affect the formation of solid-solution in binary alloy systems containing one major(solute) and one minor(solvent) element are:

- (1) The size of the component atoms. The atomic size difference should be below 15%
- (2) Crystal structures of both major and minor element should match
- (3) Valence state of the elements should be the same
- (4) Elements with similar electronegativity

The case of high entropy alloys is different from the common alloys as there are more principal elements i.e., no major or minor elements present in the system. The elements have the same probability of occupying the lattice sites to form the solid solution. So, all the elements present are to be considered as solute atoms. To incorporate the rule of sizes from Hume-Rothery principles, the parameter 'Delta' is defined to obtain the comprehensive effect of atomic-size difference in the case of multi-component alloy systems. The value of the parameter Delta can be obtained by using the equation (6) [4][6]

$$\text{Delta } (\Delta) = \sqrt{\sum_{i=1}^N C_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (6)$$

where, N is the number of components in the system, C_i is the atomic percentage of the i th component, r_i is the atomic radius and $\bar{r}$ is the average atomic radius.

From the values of ΔH_{mix} and Delta obtained from the reported literature, a phase formation map is plotted to compare the relation between the enthalpy of mixing and Delta as seen in Figure 3.

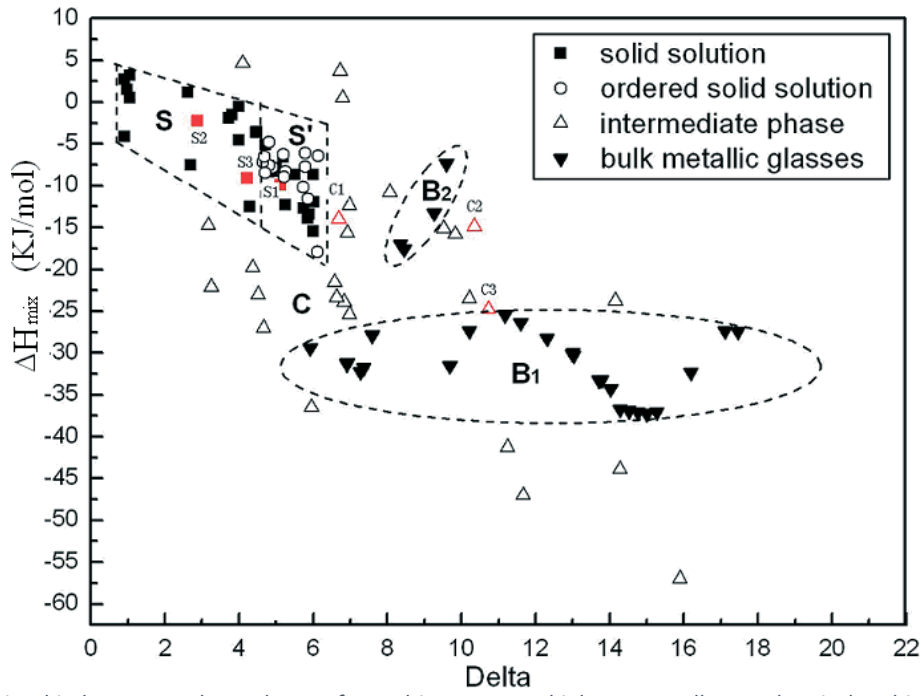


Figure 3 Relationship between Delta and ΔH_{mix} for Multi component high entropy alloys and typical multicomponent bulk metallic glasses. (NOTE TO THE SYMBOL: "solid solution" indicates the alloy contains only solid solution, "ordered solid solution" indicates minor ordered solid solution precipitate besides solid solution, and "intermediate phase" indicates there is precipitation of intermediate phases like intermetallics in HEAs. Red sign represents the alloys designed to verify the phase formation rules for multi-component HEAs)[4][6]

In Figure 3, in the zone marked as S, only solid-solutions will form as the atomic size difference is relatively small, the elements present in the system easily substitute each other to form solid solution. The value of ΔH_{mix} is not negative enough for the alloys to form a compound.[6]

In the zone marked as S', Multi component high entropy alloys form solid solutions in majority with small amounts of ordered solid solution precipitates. When compared to zone S, the Delta value increases and the enthalpy of mixing decreases which are the cause of precipitation of ordered solid solution. [6]

In zones B₁ and B₂, multi component bulk metallic glasses form rather than multi component high entropy alloys owing to the larger Delta and more negative ΔH_{mix} values in comparison to zones S and S'. In the zones marked as C, the system of high entropy alloys has intermetallic phase formation.[6]

Another plot was made to incorporate the values and effect of ΔS_{mix} in the phase formation map containing the values of Delta and ΔH_{mix} .

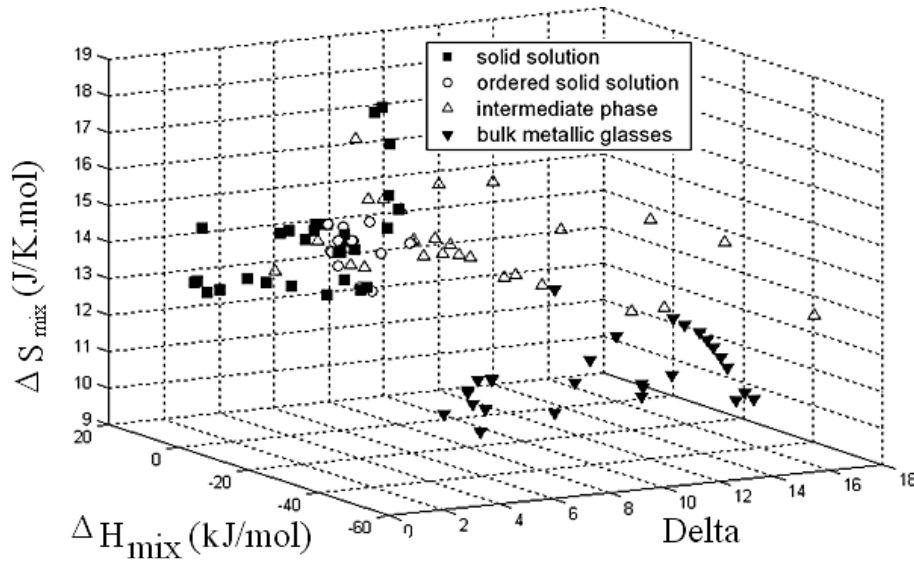


Figure 4 The Effect of ΔS_{mix} on the phase formation of the Multi component High entropy alloys and typical multicomponent bulk metallic glasses.[6]

From Figure 4, it is evident that the multi component high entropy alloys that form solid solutions have the mixing entropy values in the range of 12 J/K mol – 17.5 J/K mol. The corresponding values of Delta and ΔH_{mix} are similar to a large extent to the values observed in Figure 3. For the similar values of entropy range mentioned above, as the Delta value increases, the alloy contains ordered solid solutions and intermetallic phases. For the lower mixing entropy values and larger Delta values, multi component bulk metallic glasses form.[6]

From Figure 3 and Figure 4, we can obtain the range of values for mixing entropy (ΔS_{mix}), enthalpy of mixing (ΔH_{mix}) and atomic size difference parameter (Delta) for which the multi component high entropy alloys contain solid solution phases which contribute to the design principles of high entropy alloys.

The range of mixing entropy (ΔS_{mix}) is 12 – 17.5 J/K mol. From equation (4) and Figure 2 the minimum number of elements (N) in a system to become a high entropy alloy system can be calculated and comes to be 5.

With above discussion and values obtained, the design principles for high entropy alloys which are the modification of Hume-Rothery rule can be stipulated as:

- (1) The alloy system must contain N principal elements with $N = 5$
- (2) The atomic size difference parameter Delta should be less than 8%
- (3) Enthalpy of mixing should be in the range of -15 kJ/mol and 5 kJ/mol
- (4) Crystal structures of the elements need not match. Mixtures of elements that have BCC, FCC or HCP in their pure elemental form are frequent
- (5) Similar electronegativity is not necessary

2.2. Core effects

The compositions of the high entropy alloys are complex when compared to conventional alloy systems due to the equi-molar concentration of each element. Four core effects that are majorly responsible for the unique characteristics exhibited by high entropy alloys are summarized by Yeh[2].

2.2.1. High entropy effect

It was expected that the presence of a higher number of principal elements results in complex microstructures and intermetallics. As per the Gibbs phase rule, at the equilibrium conditions and under constant pressure

$$P = C + 1 - F$$

Where, P is the number of phases, C is the number of elements, F is the number of thermodynamic degrees of freedom. In case of 5 component system, the maximum number of phases to be expected are 6. However, high entropy alloys exhibit mostly simple microstructures rather than intermetallic microstructures. This effect is derived from the high entropy of the solid solution system which helps in stabilizing the simple microstructures. Intermetallics have a low configurational entropy as they are ordered structures. This does not imply that all the alloys in the centre of the phase diagram of multi-component system have simple microstructures as explained in section 2.1. Only HEA systems that comply with the extended design parameters form simple solid solution phases instead of intermetallic phases.[2][3][4][6]

2.2.2. Lattice distortion

As the multi component alloy system of HEAs form solid solution phases, extending the existing crystal structure concept to incorporate the HEA systems assuming random distribution of elements can be depicted by Figure 5.

Based on Figure 5, one can conclude that the lattice is heavily distorted due to the difference in the atomic sizes of the elements present in the lattice. This heavy lattice distortion can have much influence on mechanical, thermal, electrical, optical and chemical behaviour of the alloy. For sufficiently large difference in the atomic sizes of the elements can also result in formation of amorphous structures.[2][4]

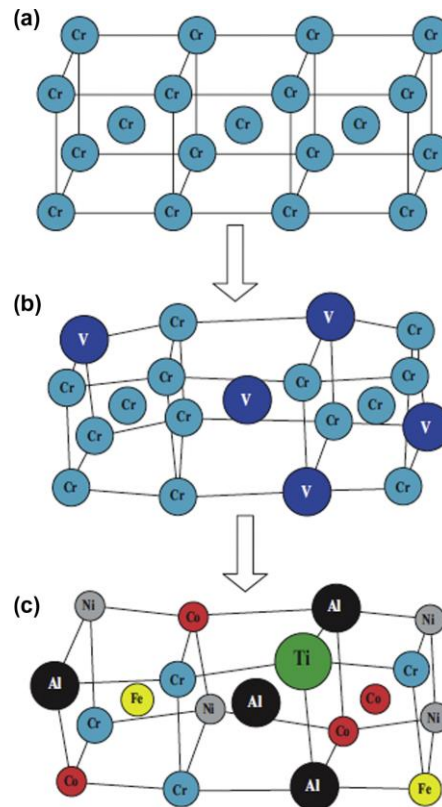


Figure 5 Schematic illustration of BCC crystal structure: (a) perfect lattice (take Cr as example); (b) distorted lattice caused by additional one component with different atomic radius (take a Cr-V solid solution as example); (c) serious distorted lattice caused by many kinds of different-sized atoms randomly distributed in the crystal lattice with the same probability to occupy the lattice sites in multi-component solid solutions[4][6]

2.2.3. Sluggish diffusion

Phase transformations under different thermo-mechanical treatments rely on atomic diffusion of the elements in the system. The vacancy formation and the composition partitioning in high entropy alloys are studied by Yeh[2] and compared the diffusion coefficients of elements in pure metals, stainless steels and high entropy alloys. The comparison of the diffusion coefficients in the mentioned systems is as shown below

$$\text{High entropy alloys} < \text{Stainless steels} < \text{Pure metals}$$

As the high entropy alloy is a substitutional solid solution with equal or nearly equal concentrations of each element, the diffusion of an element is made hard due to high interactions between the principal elements.[2][7]

From the viewpoint of kinetics, long-range diffusion for phase separation was sluggish in solid solution high entropy alloys that do not possess a single principal matrix element. Difficulty in substitutional diffusion of elements in these alloys and interactions among inter-diffusing species during partitioning lower the rates of nucleation and growth, leading to the formation of nano-crystalline structures.[7] Figure 6 shows the diffraction pattern of sputtered films containing two to seven elements, which depicts the tendency of formation of amorphous structure is higher in films containing more number of principal elements since the growth and even nucleation of crystalline phases is inhibited. This tendency to form nano-crystalline or amorphous structures can be used for our advantage to achieve the desired mechanical, chemical, physical properties.[2]

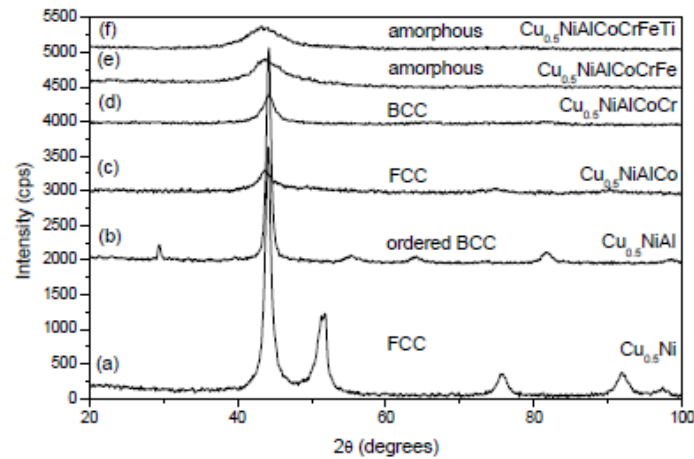


Figure 6 Structural evolution of two to seven element sputtered films analysed by x-ray diffraction[2]

2.2.4. Cocktail effects

High entropy alloys can be considered as atomic scale composite due to the presence of multiple elements in the system. The cocktail effects refer to the unique properties obtained by mixing many elements together which could not be obtained by any one independent element. Elements can be added to the system to alter the properties significantly like overall density, oxidation resistance at high temperature, solid solution hardening, promotion of the desired phase such as BCC to increase the strength of the material.[2][4]

These cocktail effects are also exhibited by conventional alloy systems but could be limited due to the minimal concentrations of alloying elements in the mixture when compared to high entropy alloys. The system of high entropy alloys also provides a large adjustment to optimize these effects due to the freedom in compositional change and alloying.

In the recent years, high entropy alloys have attracted much attention due to their unique properties, microstructures and compositions. Conventional alloy strategies generated a great understanding of the alloys having one or two principal elements but for the alloys containing several principal elements the data is virtually non-existent except for a few high entropy alloys that have been researched extensively. The following sections discuss the recent work carried out to understand the characteristics of the high entropy alloys.

2.3 Alloy preparation

The production technique used to produce an alloy system greatly influences the properties of the alloy system. This holds true for high entropy alloy systems as well. In this section, we discuss the various production techniques employed to produce high entropy alloys and the effect of these techniques on the microstructural properties of the material.[4][8]

The production techniques used can be broadly classified as:

- (1) Preparation from liquid state
- (2) Preparation from solid state
- (3) Preparation from gaseous state

Preparation of alloys from gaseous state is employed to produce thin films whereas the preparation from liquid and solid states are used to produce bulk material. In this section, we focus on the production techniques of bulk materials.

2.3.1. Preparation from liquid state

The most widely used liquid processing technique is vacuum arc melting. The torch temperature of the furnaces can be very high reaching above 3000°C and can be controlled by adjusting the power supplied. The mixing of high melting point elements can be achieved by these furnaces. But for the mixing of low melting point elements cannot be done using vacuum arc melting furnace, as the composition cannot be precisely controlled. In such cases, vacuum induction melting will be precise as the operating temperatures do not reach such high temperatures as in the case of arc melting.

High temperatures facilitate the formation of high entropy phases in liquid state. In the processing techniques employed to prepare the alloy from liquid state, kinetics plays a major role. The phase formation and microstructure of the high entropy alloys can be controlled by the cooling rate.[4]

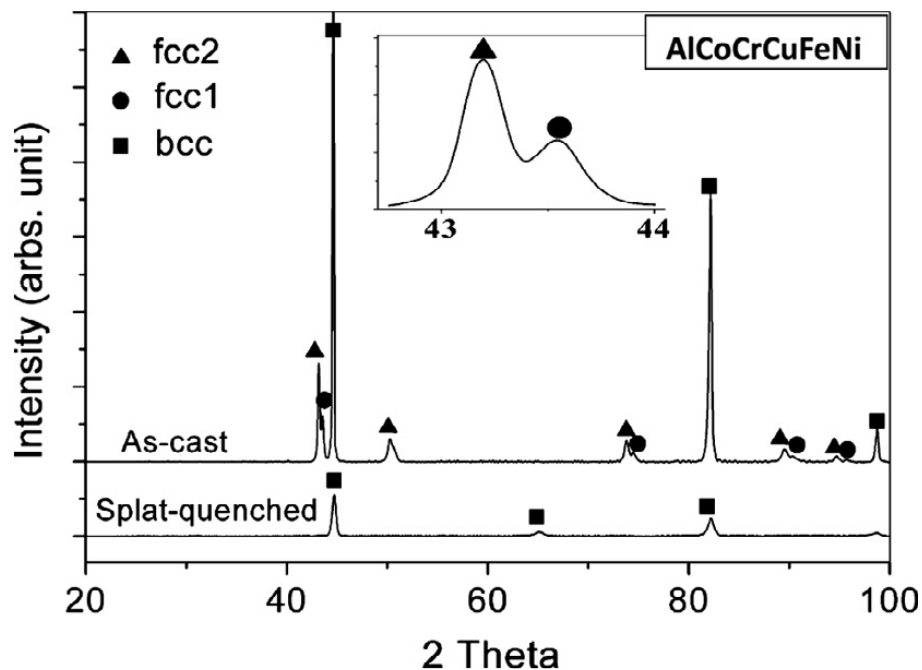


Figure 7 XRD patterns of both splat-quenched and as-cast equi-atomic AlCoCrCuFeNi HEA.[9]

In Figure 7, for the splat quenched AlCoCrCuFeNi high entropy alloy only BCC structure is observed whereas for the as cast condition, the same alloy contains BCC structure along with two FCC phases. This provides an overview that the processing technique with different processing parameters plays a vital role in phase formation.

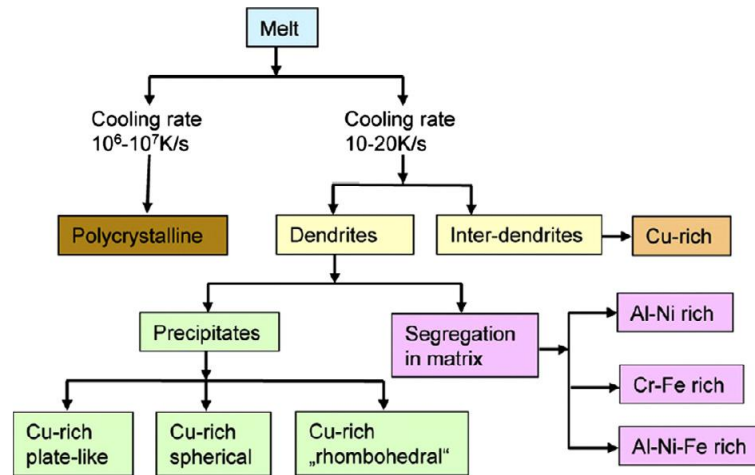


Figure 8 Schematic representation of phase segregation observed during solidification of AlCoCrCuFeNi HEA by two different processing conditions: splat quenching (10^6 - 10^7 K/s) and casting (10- 20K/s).[10]

Figure 8 depicts the study on the decomposition process of AlCoCrCuFeNi high entropy alloy carried out using two different cooling rates. The higher cooling rate promoted the formation of a single phase with polycrystalline structure while the low cooling rate resulted in the formation of different phases with different morphologies. With low cooling rate, the alloy had five phases, Cu- rich phase of L12(FCC1) in the interdendritic region, Cu- rich plate like precipitates (B2), Cu- rich rhombohedron shaped precipitates of L12 type (FCC2), Al-Ni rich plates (BCC) and Cr-Fe rich (BCC).[4][10]

Another method of preparation from liquid state is the Bridgman solidification. This method is mostly used to grow single crystal ingots. This technique involves the heating of a polycrystalline material above the melting point and slowing cooling it from one end of its diameter where the seed crystal is present. By controlling the withdrawal velocity, the properties of the material can be controlled.

The phase formation and microstructure of FeNiCrCoAl with nominal composition prepared by arc melting process and Bridgman solidification process with different withdrawal velocities ranging from $200\mu\text{m/s}$ to $1800\mu\text{m/s}$ are compared using different characterization techniques. [11]

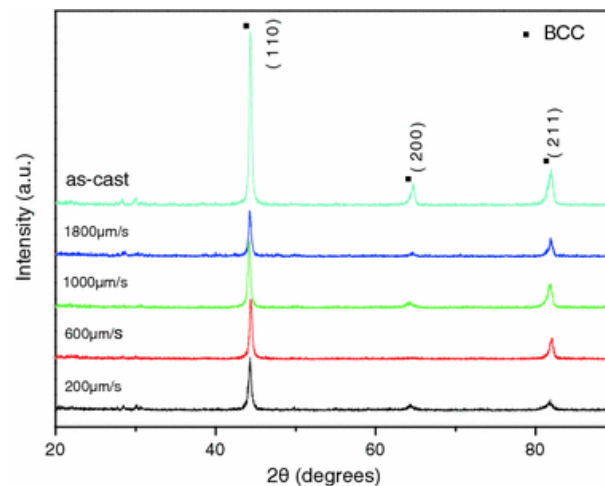


Figure 9 XRD patterns of AlCoCrFeNi HEAs of as-cast and Bridgman solidification with various withdrawal velocities of 200 to $1800\mu\text{m/s}$ [11]

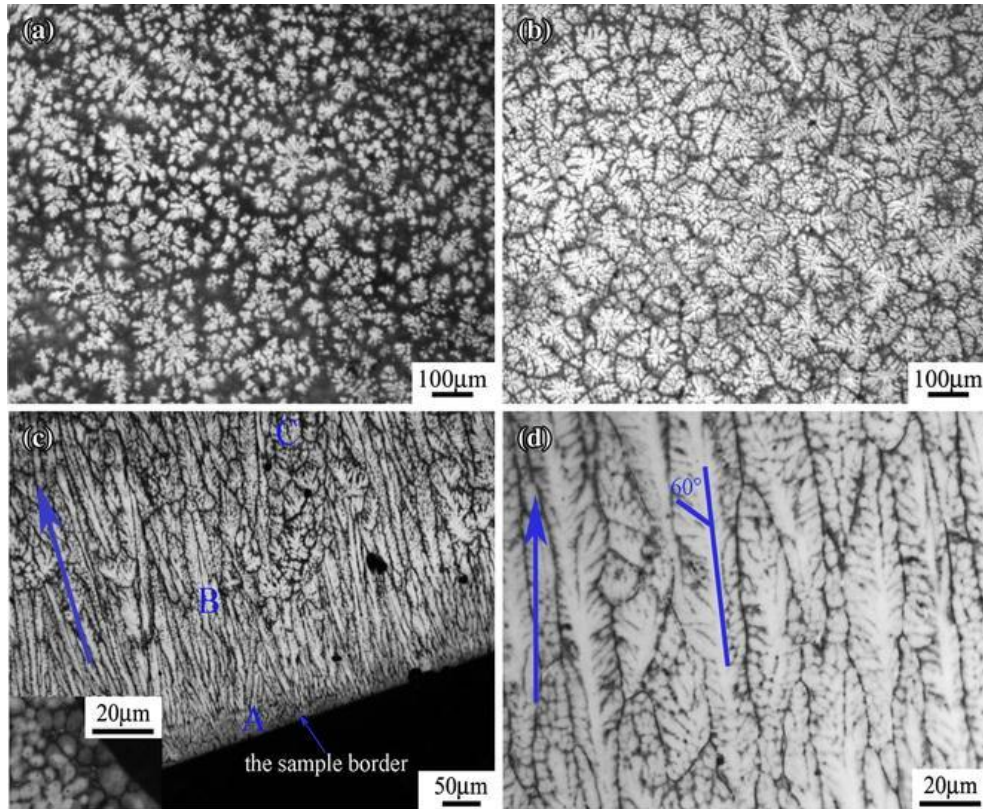


Figure 10 Metallographic photos of AlCoCrFeNi HEA cylindrical rods by copper mold suction casting: (a) and (b) dendrites viewed in the central region of the samples marked as C in (c) with diameters of 3 and 5 mm, respectively; (c) typical casting microstructures and the inset is a magnification of the finery equiaxed grains close to the sample border(location marked as A); and (d) morphology of the columnar dendrites corresponding to the B location in (c)[11]

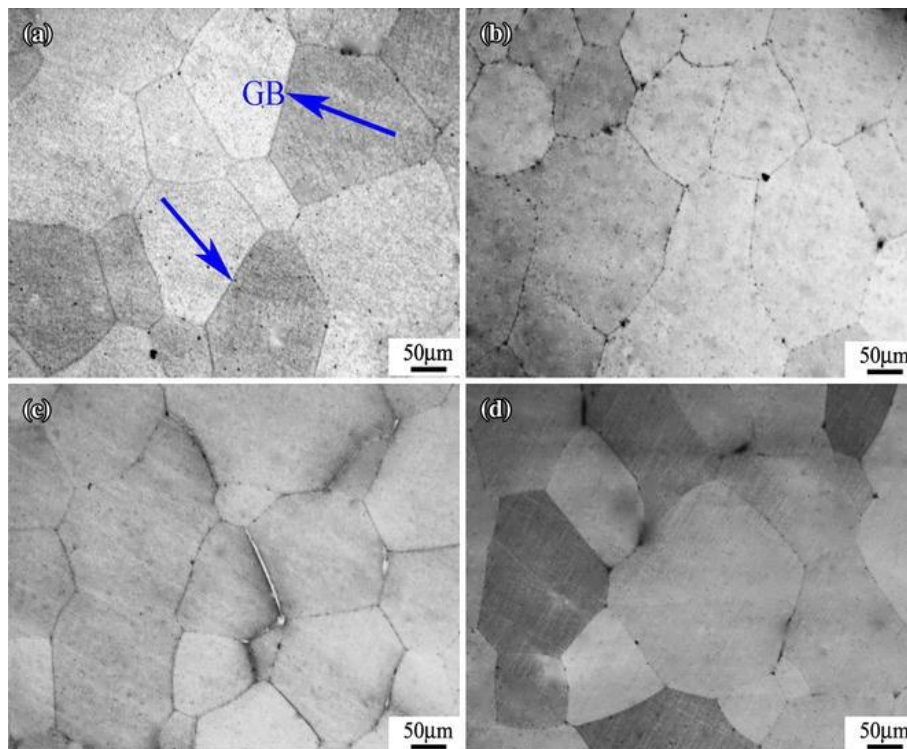


Figure 11 Metallographic photos of AlCoCrFeNi HEAs by Bridgman solidification with withdrawal velocities of (a) 200, (b) 600, (c) 1000, and (d) 1800 $\mu\text{m/s}$ [11]

XRD patterns from Figure 9 reveal the presence of single phase BCC structure in the AlCoCrFeNi high entropy alloy during every studied processing condition. Even if the same phase is present for all processing conditions, we observe difference in structure for both production techniques. Figure 10 depicts the microstructure of as cast condition in which flowery dendrites are observed in the central region with equiaxed grains at the very edge of the sample. The intermediate regions contain columnar dendrites that grow in a specific direction. On the other hand, Figure 11 shows the microstructure of the alloy after Bridgman solidification which contains equiaxed grains instead of dendrites as observed in as cast sample. The equiaxed grains can be seen for all withdrawal velocities used during the process. The grain size does not change with the change in withdrawal velocity suggesting that the AlCoCrFeNi alloy is not sensitive to withdrawal velocities.[11]

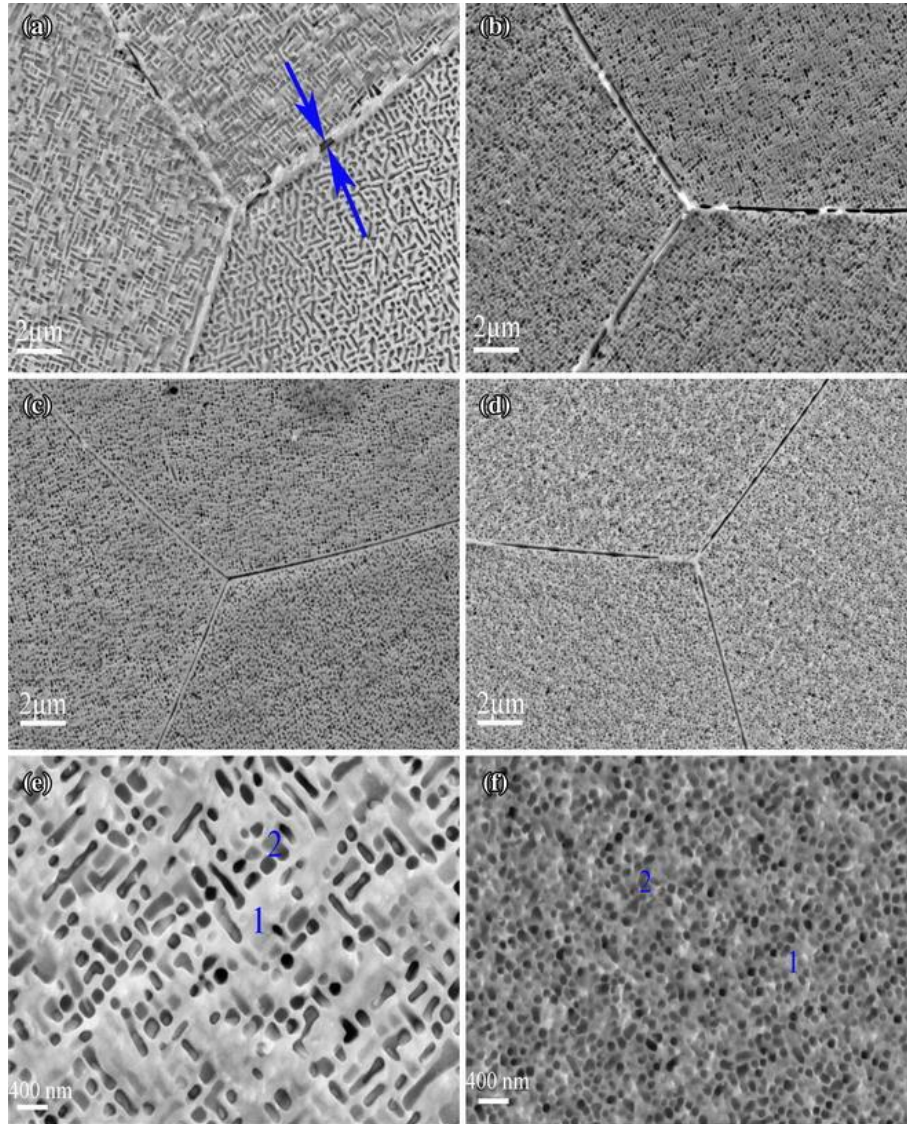


Figure 12 Secondary electron images of AlCoCrFeNi HEAs by Bridgman solidification with withdrawal velocities of (a) 200, (b) 600, (c) 1000, and (d) 1800 $\mu\text{m/s}$. (e) and (f) magnifications of (a) and (d), respectively. The arrows in (a) point out to grain boundary.[11]

Secondary electron images for the corresponding microstructures seen in Figure 11 are presented in Figure 12. Coherent and alternating platelets with different sizes, 150 to 400 nm in length and 100 to 200 nm in width are observed for the slowest withdrawal velocity of 200 $\mu\text{m/s}$. For the fast withdrawal velocity of 1800 $\mu\text{m/s}$, honeycomb like structure with uniform dispersion of spherical particles can be seen and the size of these spherical precipitates are about 50 to 100 nm. These nano scale

precipitations may be due to the spinodal decomposition leading to the structure with ordered (B2) and disordered phases (A2). This was confirmed by high energy x-ray beam measurements done at the points indicated as 1 and 2 in Figure 12 (e)(f).[11]

2.3.2. Preparation from solid state

The most used technique to prepare alloys from solid state is mechanical alloying (MA). This technique involves repeated cold welding, fracturing and rewelding of powder particles in a high energy ball mill. This technique was developed to produce oxide-dispersion strengthened nickel- and Iron- base super alloys for the use in aerospace industry.[4]

Mechanical alloying occurs in three steps.

- (1) The alloy materials are combined in a ball mill and ground to fine powders.
- (2) A hot-isostatic-pressing (HIP) process is then applied to simultaneously compress and sinter the powders.
- (3) A final heat-treatment stage helps remove existing internal stresses produced during any cold compaction, which may have been used.

In this section, we discuss various phases and microstructures obtained in high entropy alloys developed using mechanical alloying and other solid-state preparation techniques.

Preparation of FeNiCrCoAl high entropy alloy using mechanical alloying resulted in a BCC structured solid solution after 30h. This BCC structure was thermally stable up to 500°C and gradually transformed into FCC structured solid solution above 500°C.[12][13]

The other solid-state production technique in use is spark plasma sintering process (SPS). Sintering is a process of making alloys from compacted powdered elements by heating them below their melting point so that the bonding takes place by atomic diffusion.

FeNiCrCo_{0.3}Al_{0.7} prepared by mechanical alloying results in single phase BCC structure whereas preparation using spark plasma sintering process results in a partial transformation of BCC structure to FCC structure.[13]

2.4. Mechanical behaviour

With the continuous technological advancement in the world, there is a high demand for superior materials to work under extreme conditions. Some of the potential applications for high entropy alloys can be found in nuclear, automotive and aerospace industries. High entropy alloys are reported to have high hardness and compressive strength properties at both high temperatures and at room temperature. The structure types are one of the dominant factors in controlling the strength and hardness of the alloys. It is studied and reported that the high entropy alloys exhibit high strength and low plasticity for BCC structured alloys and FCC structured high entropy alloys exhibit low strength and high plasticity.

Apart from the structure dominance on mechanical properties, processing techniques, minor alloying additions and annealing treatments also play an important role in determining the mechanical properties of the high entropy alloys.

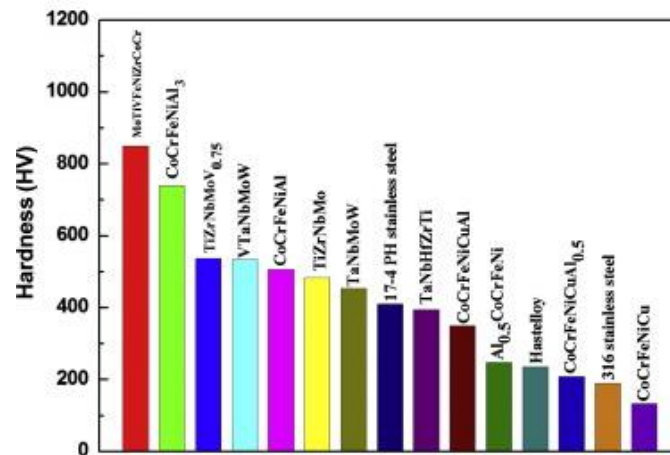


Figure 13 Wide range of hardness for HEAs, compared with 17–4 PH stainless steel, Hastelloy, and 316 stainless steel[4]

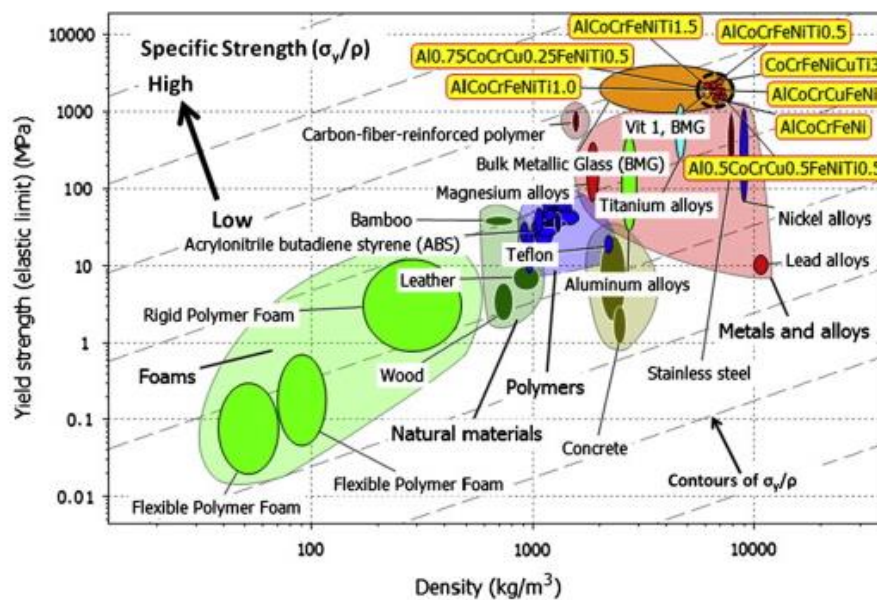


Figure 14 Yield strength, σ_y , vs. density, ρ . HEAs (dark dashed circle) compared with other materials, particularly structural alloys. Grey dashed contours (arrow indication) label the specific strength, σ_y/ρ , from low (right bottom) to high (left top). HEAs are among the materials with highest strength and specific strength[4]

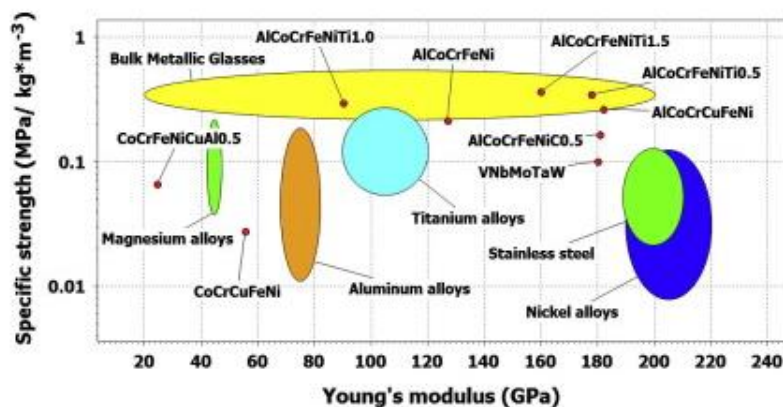


Figure 15 Specific-yield strength vs. Young's modulus: HEAs compared with other materials, particularly structural alloys. HEAs are among the materials with highest specific strength and with a wide range of Young's modulus[4]

Figure 13, Figure 14 and Figure 15 provide a general idea of where these high entropy alloys fit in regard to the mechanical properties of a material. It is also evident from the above figures is, not every combination of high entropy alloy gives good results compared to conventional alloys. So, careful selection of high entropy alloys is to be done to bring out the best possible replacements. In recent years, extensive research conducted on high entropy alloys to determine their mechanical properties.[4]

2.4.1 Effect of processing methods

As discussed in the previous section, processing technique controls the phase formation which in turn controls the properties of the alloy. In this section, we focus on the mechanical properties of the alloys prepared by various production techniques.

FeNiCrCoAl high entropy alloy prepared by mechanical alloying discussed in previous section resulted in BCC structure with high Vickers hardness of 625HV and 1907MPa compressive strength.[12]

Mechanical properties of FeNiCrCoAl high entropy alloys with different compositions were prepared by arc melting and spark plasma sintering process techniques are compared as seen in Figure 16.

Alloy	Process	σ_y (MPa)	σ_{max} (MPa)	ϵ_p (%)	Hardness (H_v)
FeNiCrCo _{0.3} Al _{0.7}	SPS	2033 ± 41	2635 ± 55	8.12 ± 0.51	624 ± 26
FeNiCrCoAl	Arc-melting	1251	2004	32.7	-
FeNiCrCoAl _{0.25}	Arc-melting	-	-	-	110 ± 2
FeNiCrCoAl _{0.5}	Arc-melting	-	-	-	159 ± 2
FeNiCrCoAl _{0.75}	Arc-melting	-	-	-	388 ± 5
FeNiCrCoAl _{0.875}	Arc-melting	-	-	-	538 ± 12
FeNiCrCoAl ₁	Arc-melting	-	-	-	484 ± 26
FeNiCrCoAl ₂	Arc-melting	-	-	-	509 ± 27

Figure 16 Mechanical properties of different FeNiCrCoAl HEA systems at room temperature[13]

The highlighted values in Figure 16 shows the difference in hardness values for the alloys with almost same composition suggesting an influence of processing technique on the mechanical properties of the material.

Comparison of AlCoFeMoNiTi high entropy alloy synthesized using arc melting and sintering processing techniques shows Mo-rich and Ti- rich phases present in arc melted sample with hardness value of 652HV while Ti-rich nano precipitates were observed in sintered sample with hardness value of 887HV.[14]

Apart from the processing techniques involved, thermo-mechanical processing of the alloy produced can greatly influence the mechanical properties of the alloy by altering the properties such as stress concentration, deformation in microstructure, recrystallization and stress relaxation in the material.

High entropy alloy CrCoFeNiMn with nominal composition was prepared by arc melting process in the shape of a bar. Discs of 10mm diameter and 1mm thickness were prepared for the High Pressure Torsion (HPT) processing. HPT was carried out at room temperature using an applied pressure of 6GPa and a rotation speed of 1rpm through 1, 5 and 10 rotations. The hardness measurements were carried out on the randomly selected diameters of the discs and can be seen in Figure 17.[15]

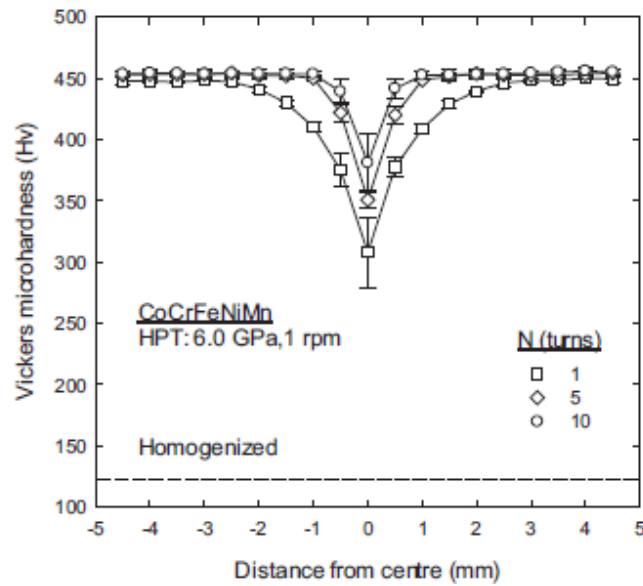


Figure 17 Values of the Vickers microhardness measured across disks processed from 1 to 10 turns at a rotation speed of 1 rpm: the lower dashed line shows the homogenized initial condition.[15]

From Figure 17, it is evident that the hardness values increase with the number of turns used in the HPT process which suggests the dependence of hardness values on the deformation in the material. For the annealing treatments, discs under 5 turn HPT process were selected and annealed for a range of temperatures (473 – 1173K) for time ranging from 10 to 60 min.[15]

Figure 18 (a), shows the phase formation during the HPT processing and different annealing conditions. The alloy contains single phase FCC structure after HPT processing which transforms into a two-phase system with FCC and BCC phases for the annealing treatments carried out at 473K, 673K and 773K for 60 min. Corresponding to these phase changes, we can observe an increase in the hardness values in Figure 18 (b). Further increase in annealing temperatures to 873K and 973K transforms the material to a three-phase system due to the formation of sigma phase in addition to BCC and FCC phases. For the annealing temperatures of 1073K, sigma phase is dissolved into the system resulting the formation of two phase system with BCC and FCC structures and for the final treatment at 1173K, FCC phase dissolves into the matrix of BCC and the material is reverted to its initial condition of HPT with single phase BCC structure.[15]

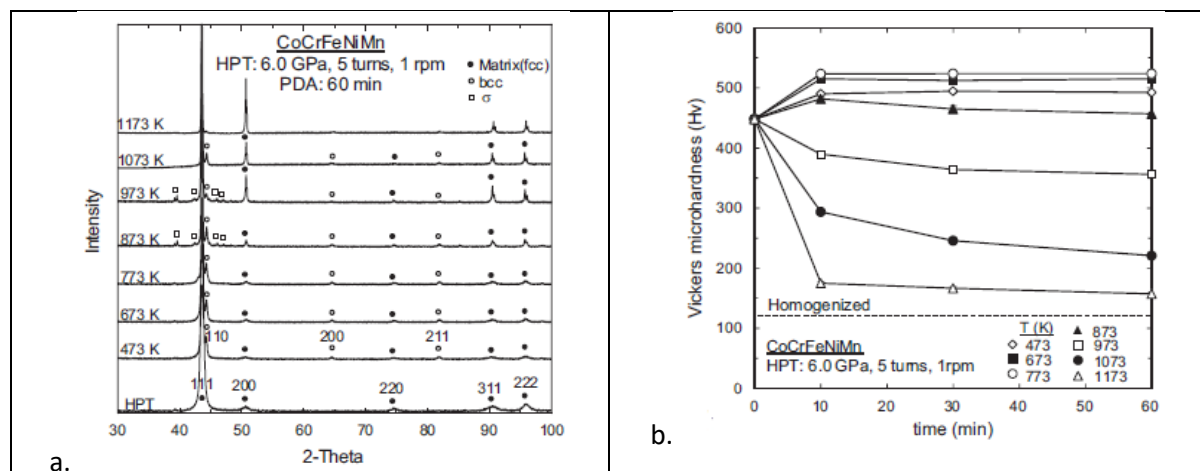


Figure 18 a. X-ray patterns near the edges of disks after HPT processing followed by PDA at 473–1173K for 60min b. Dependence of Vickers hardness of the HEA after HPT on the annealing time at different annealing temperatures[15]

The drop in the hardness values for annealing temperatures from 973K to 1173K can be explained with the help of microstructural analysis as can be seen in Figure 19.

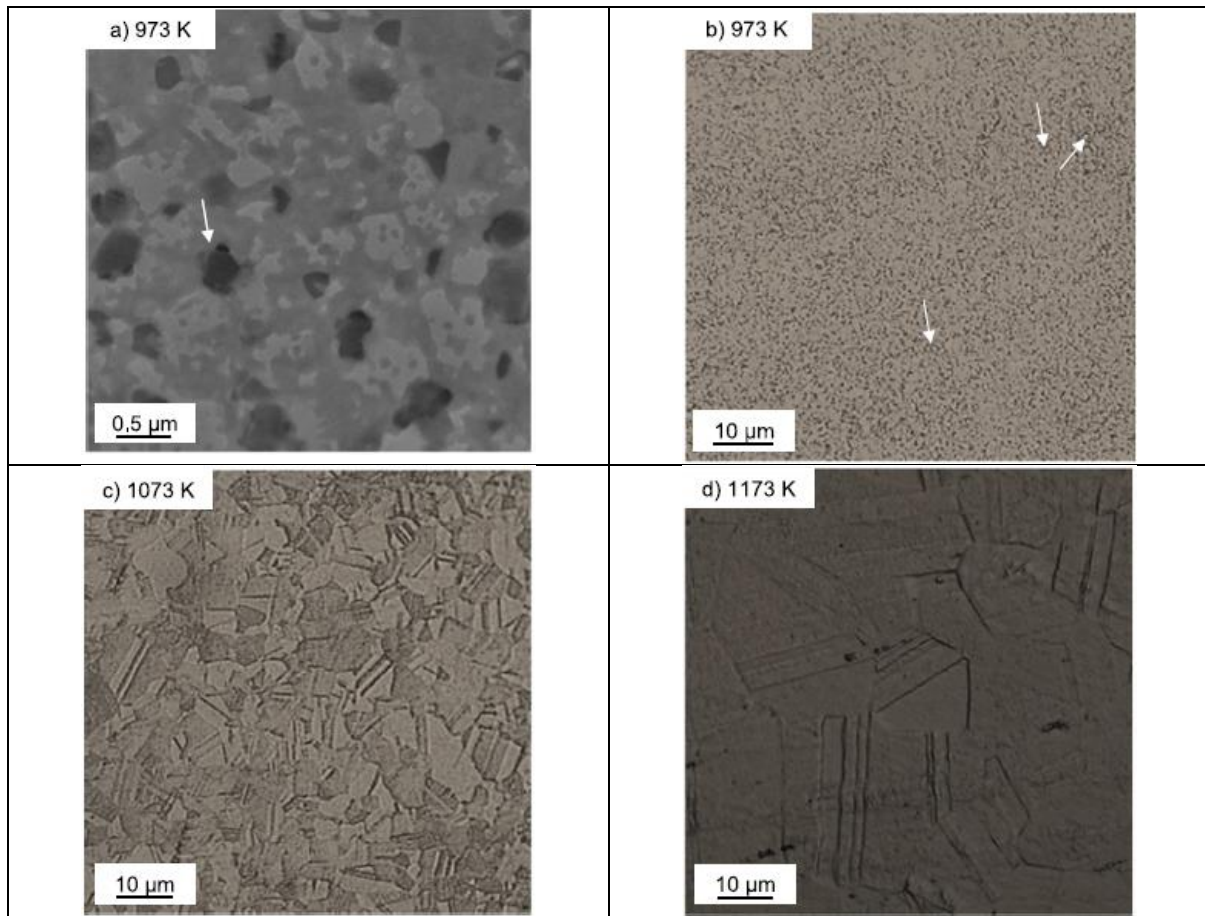


Figure 19 (a) SEM observation after annealing at 973K; arrow shows precipitated phase in the matrix. (b-d) Optical microscopy observation after annealing at 973K – 1173K. arrows in (b) show ultra-fine grains.[15]

From Figure 18 and Figure 19, the decrease in hardness can be explained as an effect of recrystallization and precipitate dissolution in the material for temperatures above 973K.

2.5 Effect of alloying elements

As in the case of conventional alloying strategy, minor addition of alloying elements is done to better suit the requirements of the applications. In the same way, minor alloying additions can be done in high entropy alloys. In this section, we focus on some of the effects of alloying elements in addition to processing techniques on the phase formation and mechanical properties of high entropy alloys.

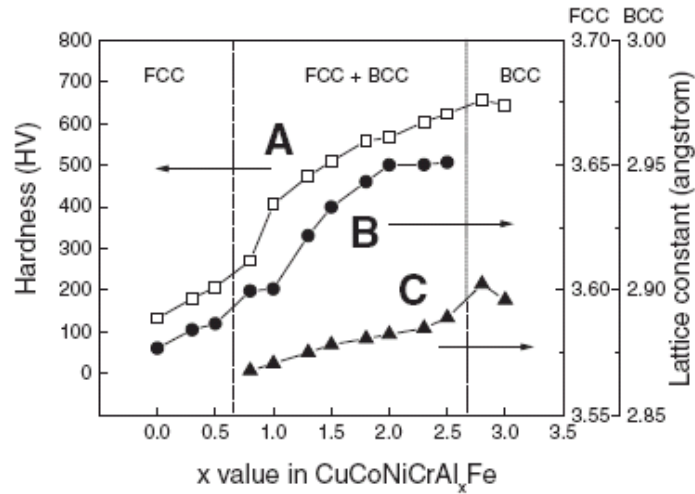


Figure 20 Strengthening effect of aluminium addition on the cast hardness of $Al_xCoCrCuFeNi$ alloys. A, B and C refer to the hardness, FCC lattice constant and BCC lattice constant respectively.[2]

Figure 20 depicts the effect of Al- addition to the $CuCoNiCrFeAl_x$ high entropy alloy on the phase formation and hardness values. It is observed that with increasing Al- concentration in the alloy, hardness of the material increases with the nucleation and growth of BCC structure in the alloy. For low concentrations ($x < \sim 0.7$) of aluminium, the alloy is a single-phase FCC system. For the aluminium concentrations ranging from $0.7 < x < 2.7$, the alloy system contains both FCC and BCC structures. For higher concentrations ($x > \sim 2.7$), the alloy system becomes a single-phase BCC.

$Al_x(NiCrCoFe)_{1-x}$ ($x = 10, 15$ and 30 at%) were prepared using arc melting process in a water cooled copper hearth furnace under argon atmosphere[16]. The as cast microstructures of these high entropy alloys were observed and presented in Figure 21.

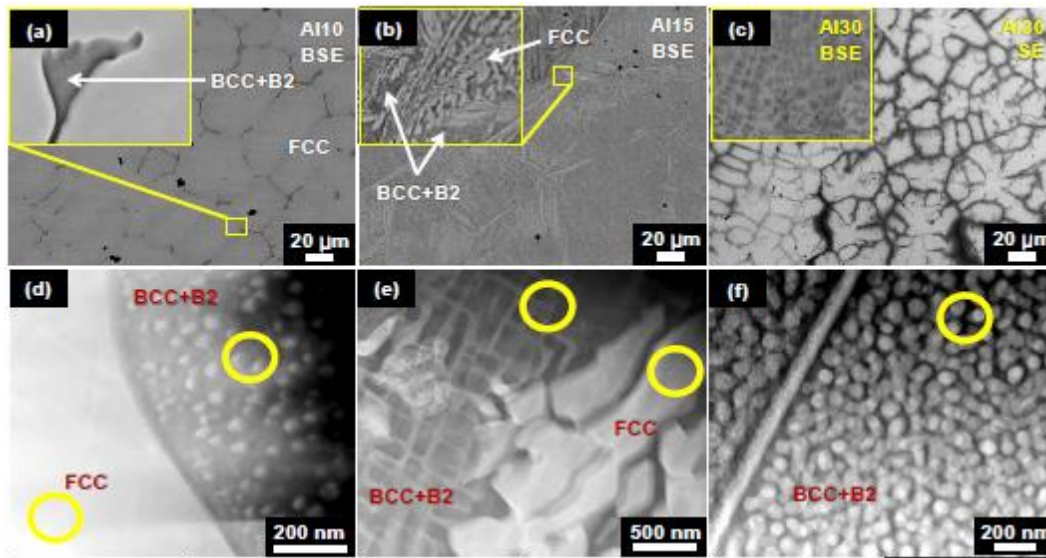


Figure 21 Representative scanning electron images (a)-(c), STEM-HAADF images (d)-(f), of the as-cast Al_{10} , Al_{15} , and Al_{30} HEAs, respectively.[16]

From Figure 21, high entropy alloy with 10 at% Al- contains FCC matrix and Ni/Al enriched BCC+B2 interdendritic regions. With the increase of Al- concentration to 15 at%, microstructure reveals heavily coarsened structure with combination of FCC and Ni/Al enriched BCC+B2 regions. High entropy alloy with 30 at% Al- contains fine scale distribution of BCC+B2 phases with no FCC regions.[16]

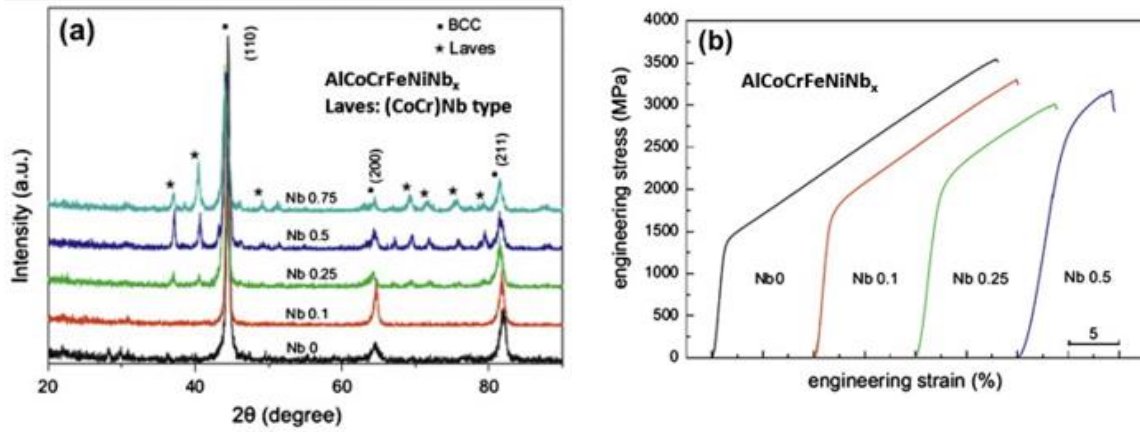


Figure 22 (a) The addition of Nb elements into this HEA changes the original phase constitution, which yields the formation of ordered Laves phase besides solid solution phase. (b) The compressive stress–strain curves of the AlCoCrFeNiNb_x rod samples with a diameter of 5 mm ($x = 0, 0.1, 0.25$, and 0.5)[17]

Figure 22 (a) shows the effect of Nb- alloying addition on the phase formation in AlCoCrFeNiNb_x high entropy alloy. For the Nb- concentrations above 0.25 mol, we observe the nucleation of laves phase of (CoCr)Nb. The effect of nucleation of laves phase in the system on mechanical properties, in this case, compressive strength can be observed in Figure 22(b). With the addition of Nb- above 0.25 molar concentration results in the decrease of plasticity of the alloy.[17]

As discussed in the previous sections, formation of phases, microstructural and mechanical properties of these alloys are dependent on processing techniques, thermo-mechanical treatments, cooling rates and alloying elements. In this work, the study is focused on the phase formation and phase fractions in FeNiCrCo and FeNiCrCoAl high entropy alloys with equi-atomic concentrations after casting and hot rolling of the material. Heat treatments at different temperatures for different times has been performed and its effect on phase formations, microstructural properties such as recrystallization, grain size, grain growth are their influence on the mechanical property (hardness) of the material has been studied.

3. Experimental procedure

The two alloy systems selected for the study, FeNiCrCo and FeNiCrCoAl were prepared by induction melting the elements together in a cylindrical alumina crucible. The casting process was performed under vacuum and in the presence of argon atmosphere. The crucible was air cooled after casting process. This condition of the material will be referred as 'as cast' condition in the later sections. These cylindrical ingots from casting were hot rolled at 1200°C – 900°C to achieve a reduction of 90% in thickness from 30mm to 3mm. After the hot rolling process, the material was quenched in water. This condition of the material will be referred as 'as rolled' condition.

The composition of the alloys after the casting process was measured using X-ray fluorescence (XRF) technique using a Panalytical Axios Max WD-XRF spectrometer and data evaluation was done with SuperQ0.5i/Omnian software.

Samples were prepared from the cylindrical ingots and rolled sheets of the two alloys for further processing and characterization. The samples of both the alloys of both conditions (as cast and as rolled), were subjected to heat treatments for a range of temperatures for different times. The samples were quenched in water after the heat treatment. Table 2 show the heat treatment conditions that have been implemented.

Table 2 Representation of heat treatment conditions carried out in this study

Annealing Conditions				
Composition	FeNiCrCo, FeNiCrCoAl			
Starting condition	As Cast , As Rolled			
Temp/Time	16 hrs	24 hrs	48 hrs	72 hrs
600 C				
800 C				
950 C				
1100 C				
1250 C				

Samples obtained after every processing condition such as casting, hot rolling and heat treatments were embedded, polished and etched for the analysis using different characterization techniques.

The samples were embedded and sanded using Silicon carbide papers with grit sizes ranging from 180 to 2000. The samples polished using 3 μ and 1 μ diamond paste on polishing cloths mol and nap respectively. The polished samples were then etched using Marble's reagent.

Phase determination in the samples was carried out using X-ray diffraction (XRD) technique using Bruker D8 Advance diffractometer Bragg-Brentano geometry with graphite monochromator and Vantec position sensitive detector using Co-K α radiation. Data analysis was carried out using Bruker software Diffrac.EVA vs 4.2.2.

Vickers hardness values of the samples were calculated using Struers Durascan 70 hardness tester with 50N (HV5) load application.

Microstructural characterisation was carried out using Keyence VHX-5000 digital microscope equipped with magnification lenses ranging from 20x to 2500x, JSM IT-100 scanning electron microscope (SEM) equipped with tungsten hairpin filament as electron source, Everhart-Thornley secondary electron detector, Si p-n junction semi-conductor backscattered electron detector and

Silicon drift energy dispersive spectroscopy (EDS) detector and JEOL JSM 6500F (hot-Field Emission Gun) Scanning Electron Microscope (SEM). Electron Backscattered Diffraction (EBSD) data acquisition was done with the Oxford-HKL Channel 5 software (Flamenco module) using a Nordlys II detector operated at 20 kV with 2 nA beam current. The Post processing was done with Channel 5 (Tango module). Energy Dispersive Spectroscopy (EDS) was performed with a Thermo - Noran System 6 equipped with a ultradry with 40 mm² Silicon drift (SDD) detector.

4. Results and Discussion

The samples of both alloys were taken from the cylindrical ingots after casting process and composition analysis was carried out using XRF technique. The results are given in Table 3.

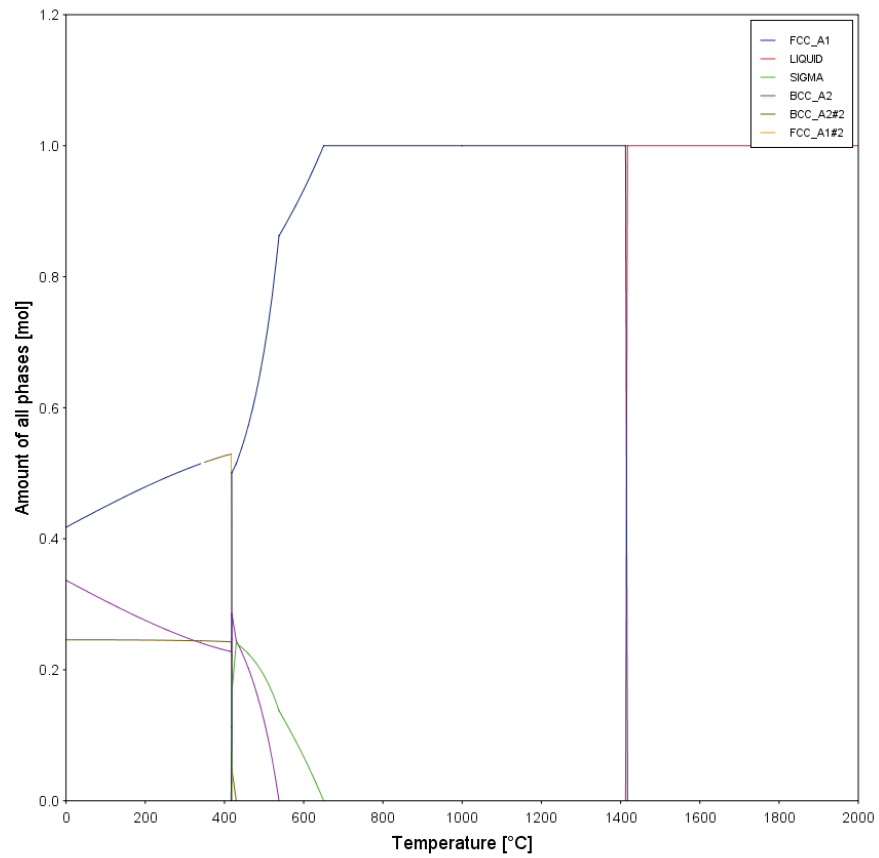
Table 3 Experimental composition distribution of the high entropy alloys in as cast condition. All quantities mentioned are in weight%.

Sample	Fe	Ni	Cr	Co	Al
FeNiCrCo	25.6 ± 0.3	26.2 ± 0.3	22.7 ± 0.2	25.3 ± 0.3	0.019 ± 0.004
FeNiCrCoAl	22.2 ± 0.3	24.3 ± 0.3	20.1 ± 0.2	23.2 ± 0.3	9.85 ± 0.09

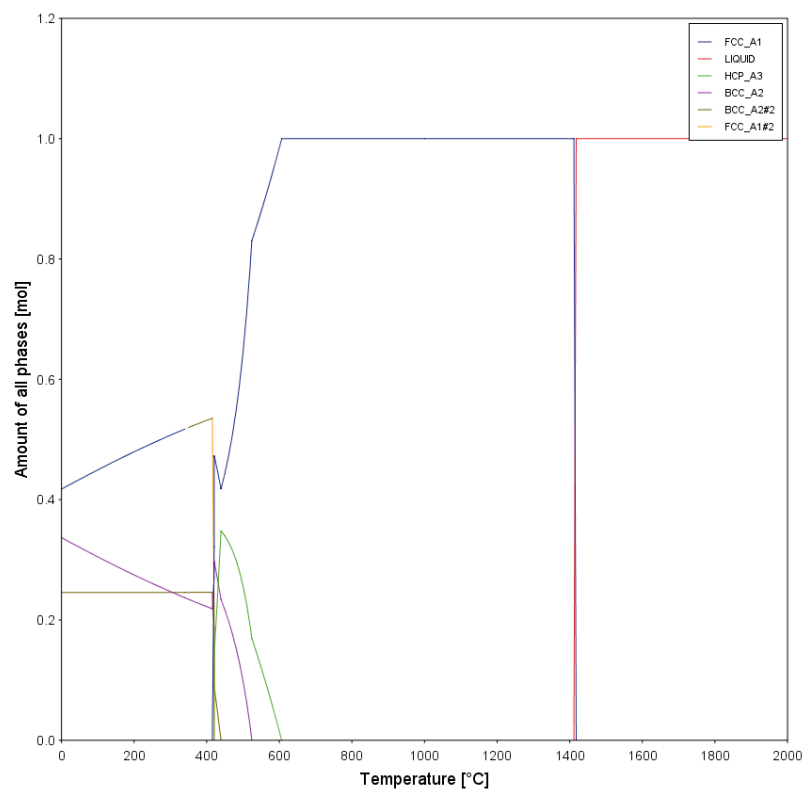
These values derived from XRF data analysis are in close range to the values presented in Table 1. The difference in the values could be from various causes such as casting defects, XRF data acquisition and analysis. Still, the experimental values are in the range of composition values expected from high entropy alloys. The minor quantity of Al present in FeNiCrCo high entropy alloy could be due to the contamination from the alumina crucible used for casting process.

Before carrying out the experimental processes mentioned in chapter 3, equilibrium phases in the alloy systems were predicted using Thermo-Calc (2017a version). There is no specific standard database for high entropy alloys in the software to predict the equilibrium phases as the Thermo-Calc data is limited to binary and ternary systems. We have used three different available databases, namely, TCFe8 – TCS Steels/Fe-Alloys database, SSOL2 – SGTE alloy solutions database v2.1 and TTNi6 – TT Ni-alloys database v6.3.

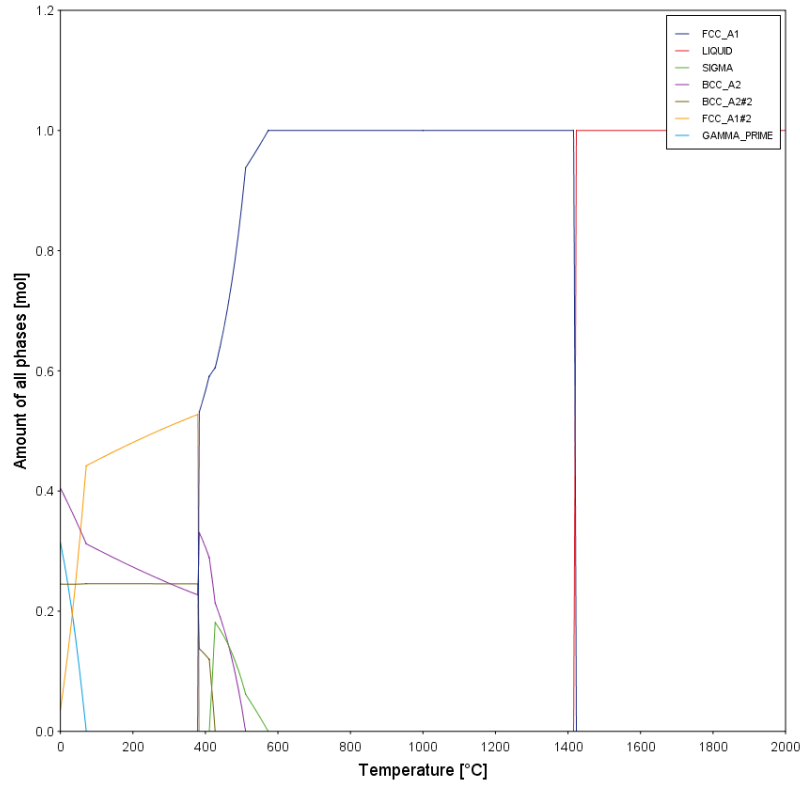
The terms BCC, FCC, HCP refer to body centered cubic, face centered cubic and Hexagonal close packed structures respectively. The terms A1 and A2 refer to disordering in the crystals and B2 refers to ordering in the crystals.



a.



b.



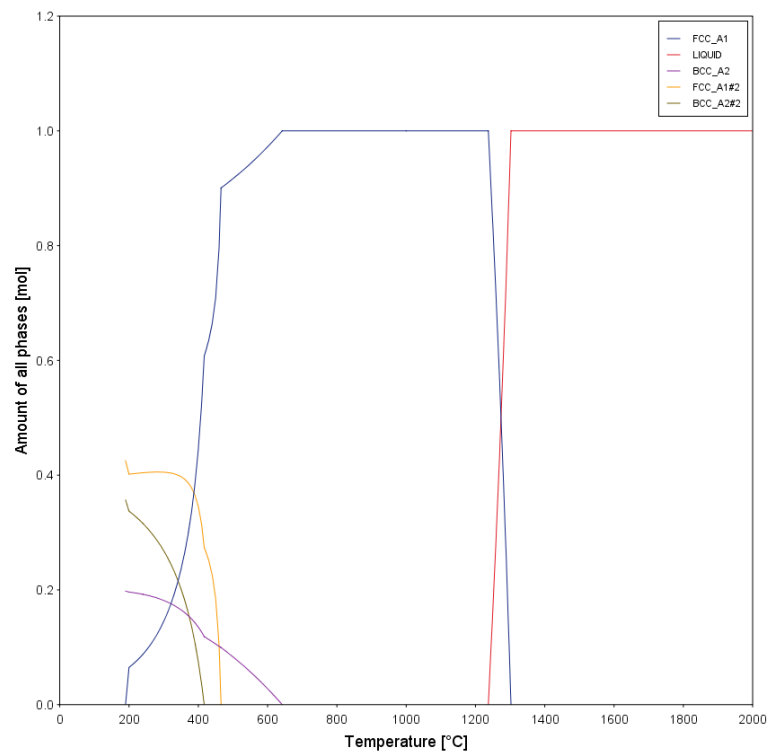
C.

Figure 23 Phase maps for FeNiCrCo high entropy alloy using a. TCFE8 database b. SSOL2 database and c. TTNi6 database using the experimental weight% values of the elements

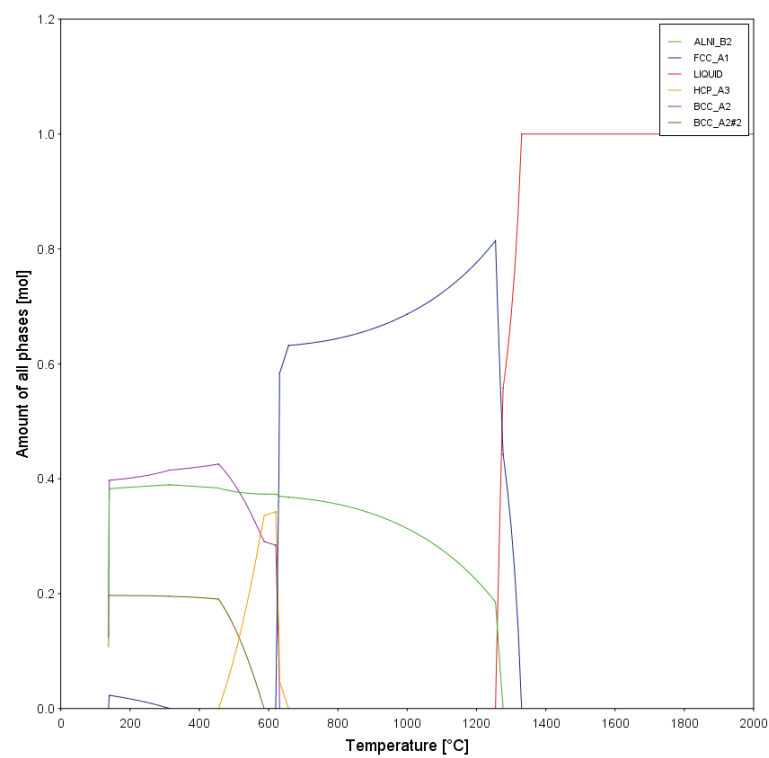
According to Table 2, the work reported in this report is focused on the temperatures ranging from 600°C to 1250°C. Figure 23 depicts the expected equilibrium phases in the FeNiCrCo high entropy alloy. In the temperature range of our interest, the alloy system as predicted by TTNi6 database has a single-phase FCC system. Database TCFE8 predicts a certain fraction of sigma phase and SSOL2 database predicts a certain fraction of HCP_A3 phase around 600°C along with FCC phase. Table 4 gives the phase fraction values of the predicted phases by each database for the temperature range.

Table 4 Phase fractions as predicted by different databases for the temperature range for FeNiCrCo high entropy alloy

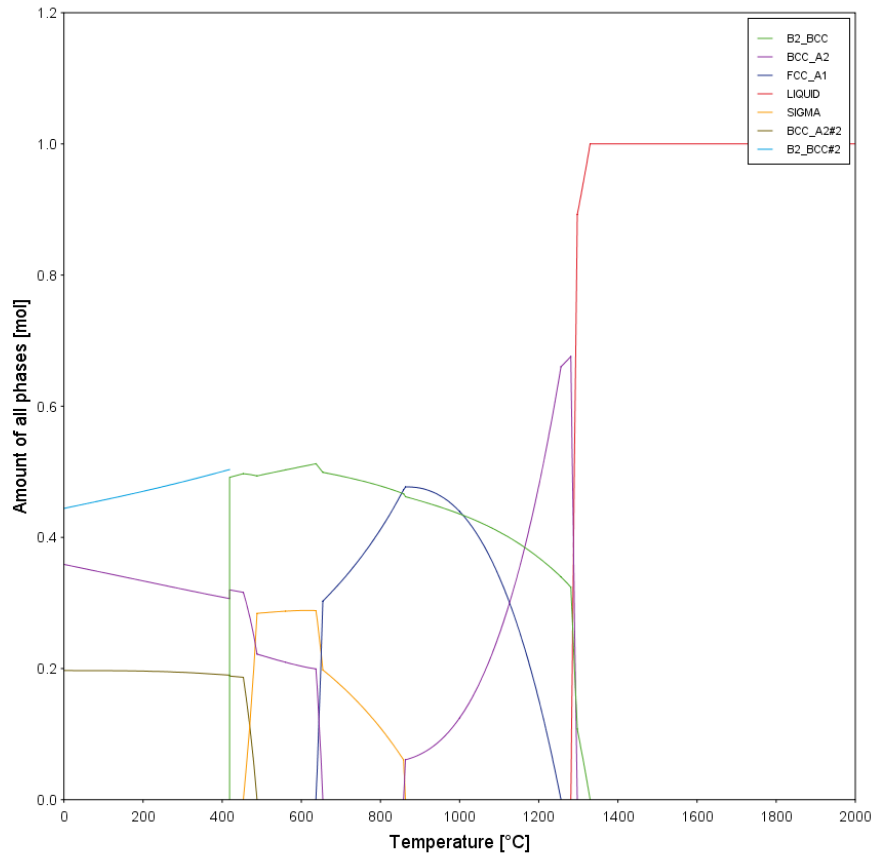
FeNiCrCo	TCFE8		SSOL2		TTNi6
	FCC_A1	Sigma	FCC_A1	HCP_A3	FCC
600°C	93	7	98.5	1.5	100
800°C	100	0	100	0	100
950°C	100	0	100	0	100
1100°C	100	0	100	0	100
1250°C	100	0	100	0	100



a.



b.



C.

Figure 24 Phase maps for FeNiCrCoAl high entropy alloy using a. TCFE8 database b. SSOL2 database and c. TTNi6 database using the experimental weight% values of the elements

From Figure 24, for FeNiCrCoAl high entropy alloy using TCFE8 database, Thermo-Calc predicts a single-phase FCC for the range of temperatures from 600°C to 1250°C with a certain fraction of BCC_A2 around 600°C. Using SSOL2 database, Thermo-Calc predicts FCC_A1, ALNI_B2 (BCC) phases with certain fraction of HCP and BCC_A2 phases around 600°C.

Using TTNi6 database, two variants of BCC (namely, BCC_B2 and BCC_A2), FCC_A1 and Sigma phases are predicted to be present in the alloy system for the focused temperature range. Table 5 gives the phase fraction values of the predicted phases by each database for the temperature range.

Binary and ternary phase diagrams with different combination of elements were obtained using TTNi6 database in Thermo-Calc. It was found that the alloy systems in combination with Al do not form sigma phase. Extrapolating this data to a higher order system containing 5 elements (Fe, Ni, Cr, Co, Al), it can be concluded that the sigma phase predicted does not contain Al.

BCC_B2 structure for a binary alloy contains one element at the center of the unit cell and the second element resides at the corners of the unit cell. Extending the concept to higher order alloy systems, we can expect one element at the center of the unit cell and the other elements reside at the corners of the unit cell in the repetitive manner producing the ordering in crystals. BCC_A2 and FCC_A1 are disordered structures with a random distribution of elements at the lattice points of the unit cell.

Table 5 Phase fractions as predicted by different databases for the temperature range for FeNiCrCoAl high entropy alloy

FeNiCrCoAl	TCFE8			SSOL2				TTNI6			
	FCC_A1	BCC_A2	Liquid	FCC_A1	AlNi_B2	BCC_A2	HCP_A3	B2_BCC	BCC_A2	FCC_A1	Sigma
600 C	97.23	2.77	0	0	37.33	28.82	33.85	50.78	20.37	0	28.85
800 C	100	0	0	64.44	35.56	0	0	47.84	0	41.22	10.94
950 C	100	0	0	67.25	32.75	0	0	44.64	8.98	46.38	0
1100 C	100	0	0	72.35	27.65	0	0	40.85	25.18	33.97	0
1250 C	83.65		16.35	81.1	18.9	0	0	34.33	63.81	1.86	0

Let us now discuss the results obtained by using different characterization techniques on the samples that underwent thermo-mechanical processing for both the alloy systems separately.

4.1. FeNiCrCo high entropy alloy

Differential scanning calorimeter (DSC) experiments were performed to detect any phase transformations that could occur over the range of temperatures that are focused on in this study. The underlying principle of this technique is that when the sample undergoes a physical change such as phase transformation during heating or cooling, the heat flow to or from the measured sample would be affected. The difference in heat flow with a reference sample is measured and reported as either endothermic or exothermic process. This gives us an indication of the phase transformations that take place in the sample.

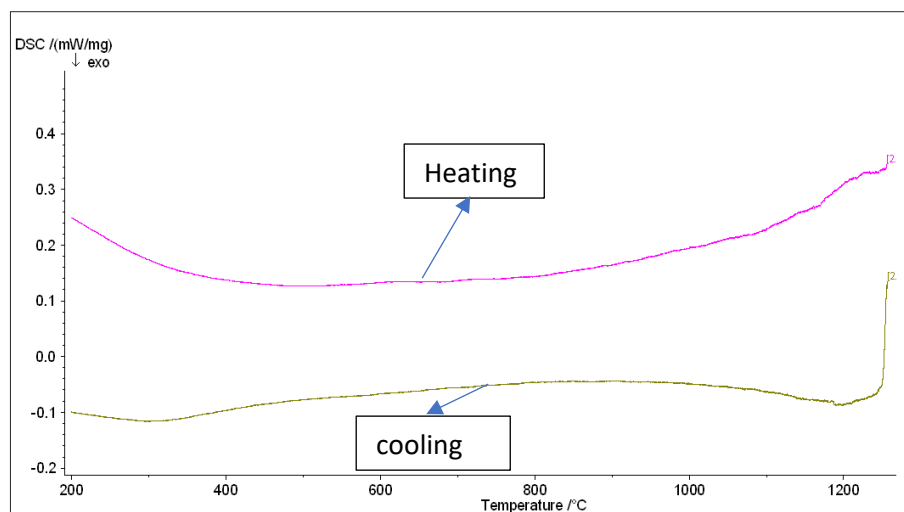
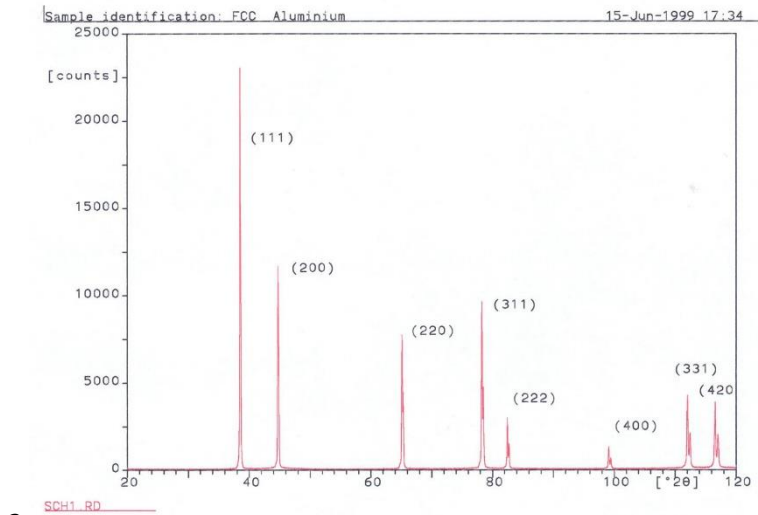


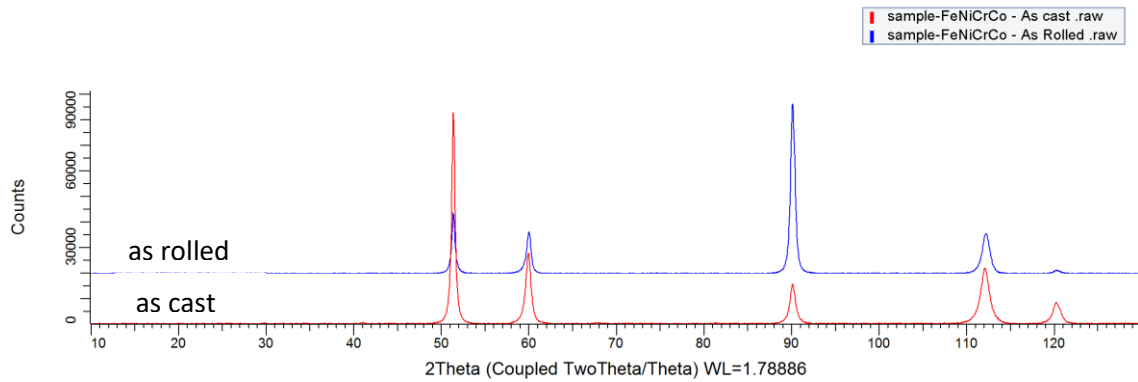
Figure 25 Differential scanning calorimeter plot for as cast FeNiCrCo HEA for the temperature range 200°C – 1250°C

Figure 25 shows that for the FeNiCrCo alloy system, there is no sudden change in heat flow recorded during both heating and cooling steps of the experiment over the whole temperature range. This suggests that there is no phase transformation that takes place in the system. So, the existence and transformation of sigma phase or HCP phase to FCC phase as predicted by TCFE8 and SSOL2 databases respectively for this alloy system around 600°C as seen in Figure 23 is not evidenced by DSC experiment.

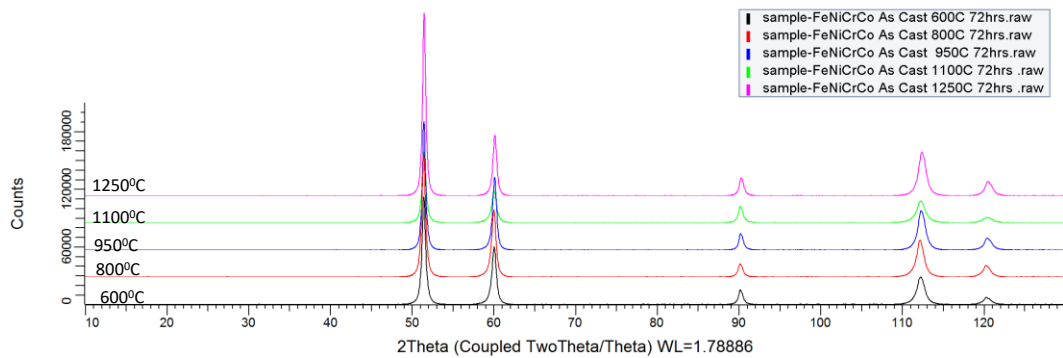
X-ray diffraction (XRD) is used to determine the phases that exist in the samples after every heat treatment.



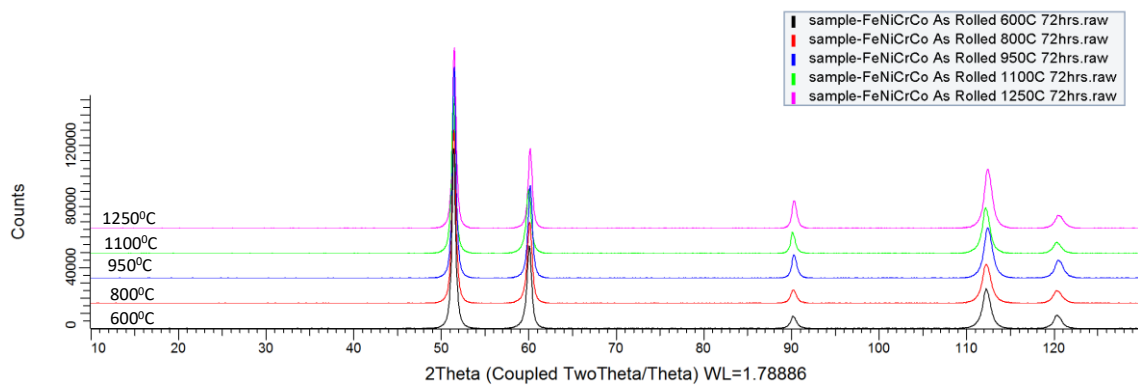
a.



b.



c.



d.

Figure 26 (a) XRD plot for pure aluminium showing the peak occurrence for FCC crystal structure denoting the planes of reflection responsible for the peak generation. Experimental XRD results depicting phases present in FeNiCrCo HEA system for (b) as cast and as rolled samples (c) XRD results for as cast condition samples after heat treatments at different temperatures for 72 hrs (d) XRD results for as rolled condition samples after heat treatments at different temperatures for 72 hrs.

From Figure 26 (a) and (b), it is observed that FeNiCrCo high entropy alloy contains single phase FCC structure in the material for both as cast and as rolled conditions. Figure 26 (c) and (d) depicts the XRD data for the samples after heat treatments at different temperatures for 72 hours. The data suggests that the alloy system does not undergo any phase transformations during the heat treatments in the samples from both as cast and as rolled starting conditions. These XRD results are consistent with the DSC experiment results where no evidence for phase transformation can be seen in the material for the whole temperature range. From the experimental results obtained from both XRD and DSC, we can conclude that FeNiCrCo high entropy alloy is a single-phase FCC system for the experimental conditions focused on in the report. In comparison between XRD, DSC and Thermo-Calc results, TTNi6 database provides closest predictions to the experimental values and could be considered as a reference database for the FeNiCrCo high entropy alloy studied in this report.

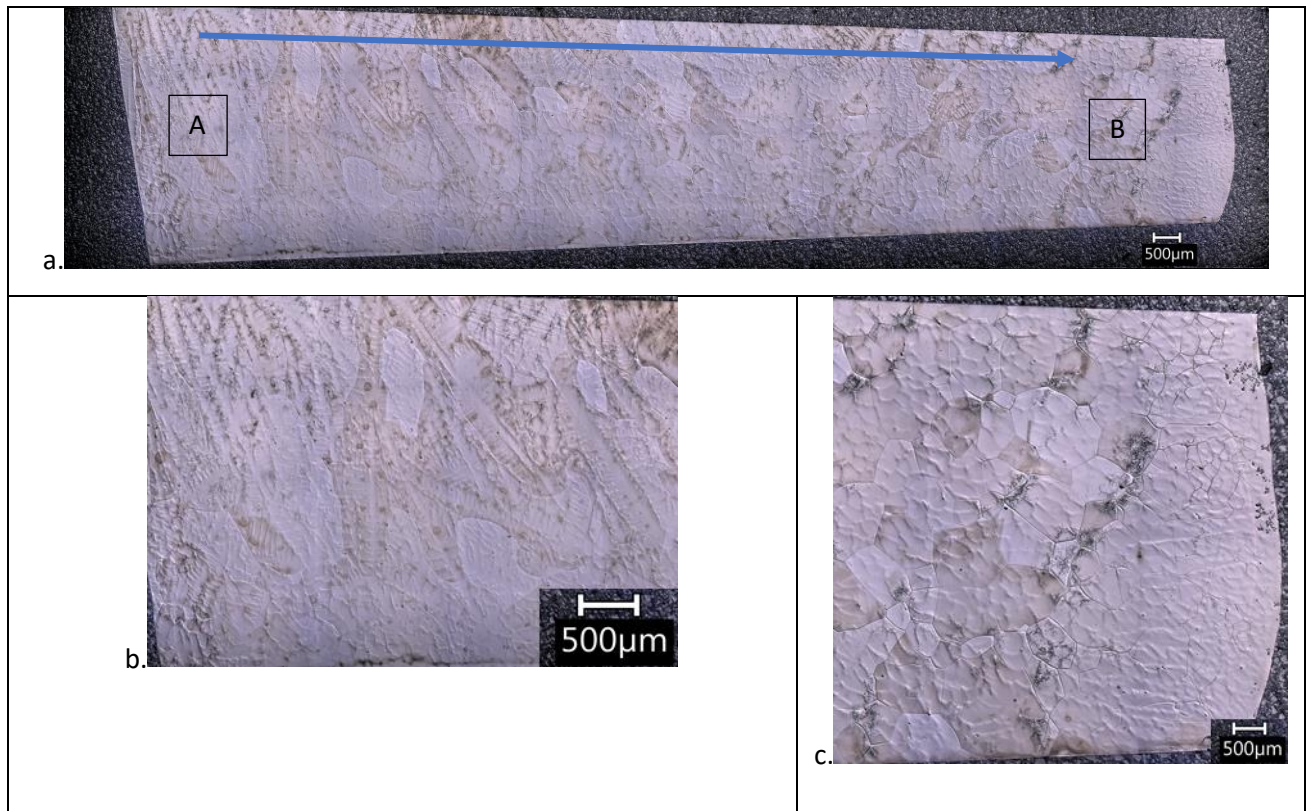


Figure 27 Optical micrographs of etched as cast FeNiCrCo high entropy alloy. (a) etched sample revealing the microstructure over the cross-section. The arrow indicates the direction from the edge to the center of the cast ingot. (b) and (c) are the magnified images of areas marked as A and B respectively.

Figure 27 depicts the as cast microstructure of FeNiCrCo high entropy alloy. The morphology is similar to the typical microstructure of conventional alloys obtained during the casting process. We observe dendrite formation in the alloy during cooling. The morphology near the edge of the cast ingot show elongated grains and towards the center of the ingot we observe equiaxed grains. The XRD results for the as cast FeNiCrCo high entropy alloy show a single-phase FCC present in the system. However, we observe the formation of dendrites which suggest the segregation of elements during cooling. So, the phases present in both dendritic and interdendritic regions are FCC with different combination of elements in the lattice resulting in the similar lattice parameter, which suggest the presence of

miscibility gap in the system for a temperature range during cooling. The length of the dendrites is in the range of 2 mm and the grain size of equiaxed grains is in the range of 600 μm .

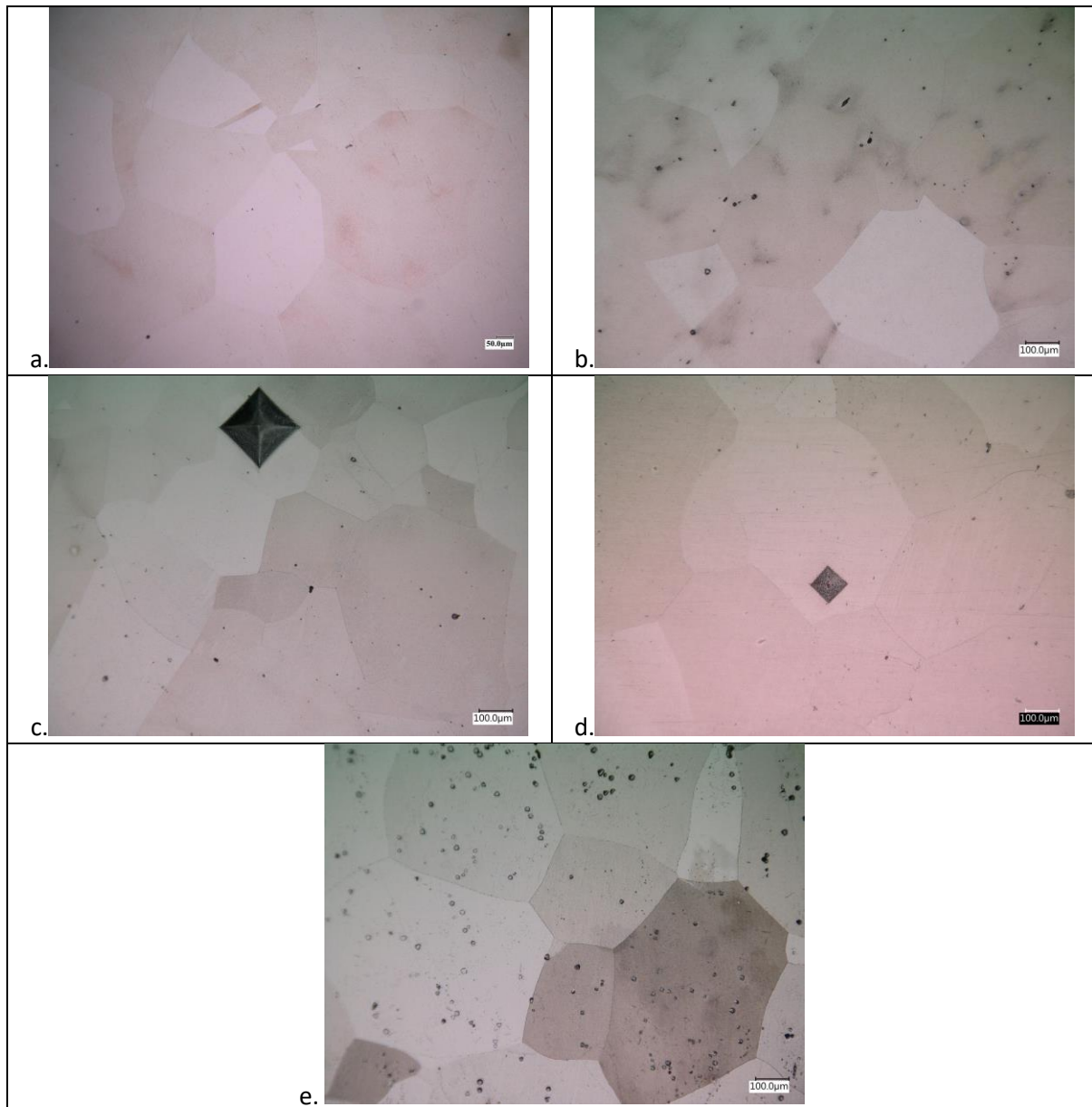


Figure 28 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after heat treatments at a. 600°C b. 800°C c. 950°C d. 1100°C e. 1250°C for 72hrs

Figure 28 (a-e) show the optical micrographs of the heat treated samples for different temperatures. It can be observed from these micrographs that the morphology from dendritic and elongated grains has changed to equiaxed grains throughout the sample after heat treatments. The average grain size in the material increases from 400 μm for 600°C heat treatment to 604 μm for 1250°C heat treatment. The sluggish diffusion property as explained in section 2.2.3 is responsible for the slow grain growth at elevated temperatures observed in the FeNiCrCo high entropy alloy.

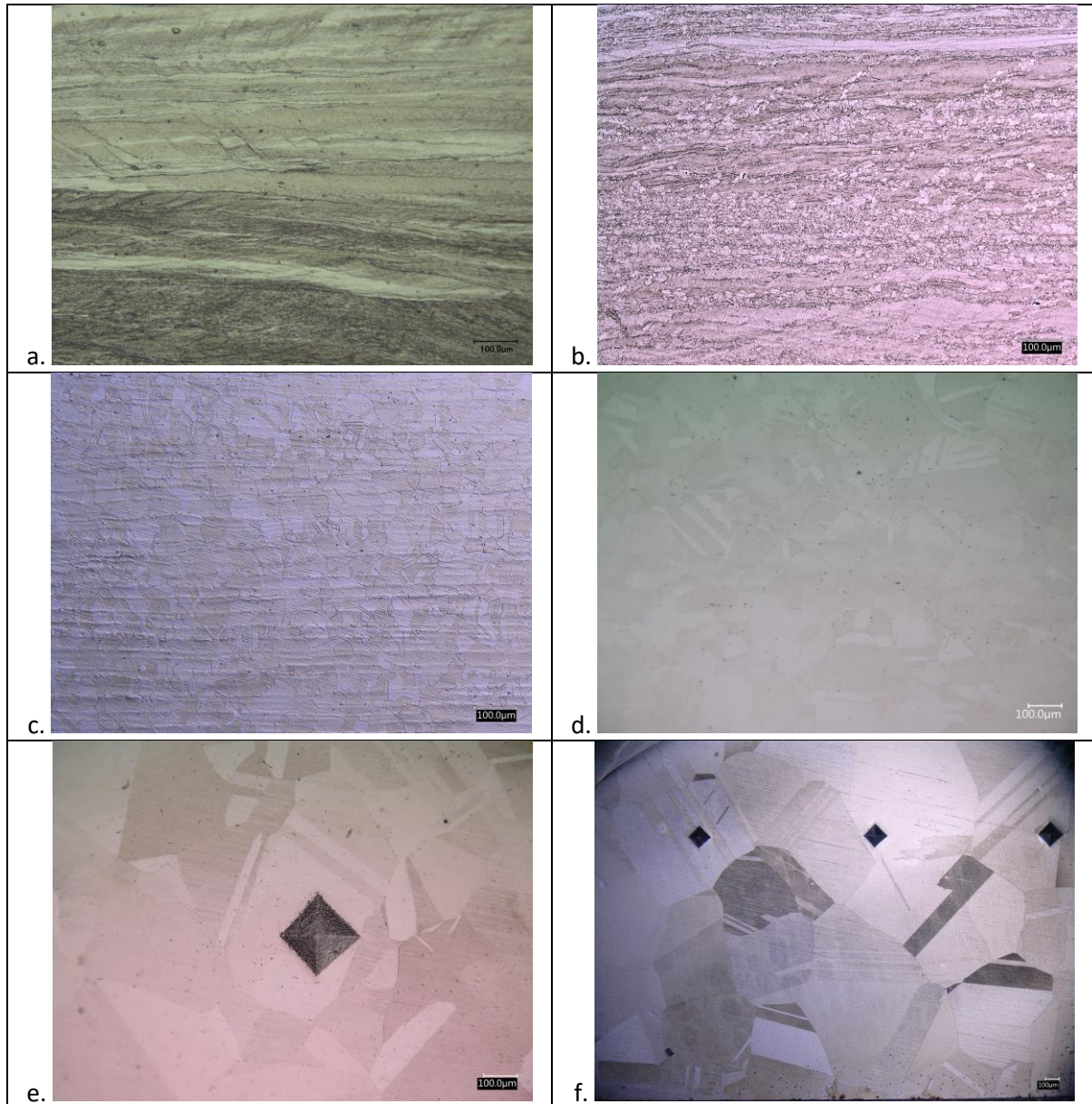


Figure 29 Optical micrographs of etched as rolled FeNiCrCo High entropy alloy for different conditions (a) As rolled condition (b-f) heat treated at 600, 800, 950, 1100, 1250°C respectively for 72 hours

Figure 29 (a) shows the deformed microstructure of FeNiCrCo high entropy alloy after hot rolling. The microstructure contains only deformed bands created during rolling and no recrystallization has taken place in the sample. Figure 29 (b-f) shows the optical micrographs of the material after heat treatments at 600°C, 800°C, 950°C, 1100°C and 1250°C respectively.

Figure 29 (b) shows the microstructure of the sample heat treated at 600°C for 72 hrs. The micrograph reveals the recrystallization and grain growth that has taken place to a small extent in the sample. Image analysis was performed by ImageJ software to calculate the percentage of recrystallization and average grain size in the sample. The fraction of recrystallization is calculated to be 45% with the average grain size of 5 µm after heat treatment at 600°C for 72 hrs. Figure 29 (c) shows the microstructure of the sample heat treated at 800°C for 72 hrs. The micrograph reveals grain growth and higher fraction of recrystallization in the material compared to the sample heat treated at 600°C. Still, the deformation bands exist, which shows that the material is not fully recrystallized. The analysis

of the image by ImageJ gave the percentage of recrystallization and average grain size value. The fraction of recrystallization is calculated to be 90% with the average grain size of 43 μm .

Figure 29 (d) shows the micrograph of the sample heat treated at 950°C for 72 hrs. The micrograph reveals full recrystallization along with grain growth occurred in the sample during the heat treatment. The average grain size for the heat treated sample at 950°C for 72 hrs is 152 μm . The grain growth continues for the samples heat treated at 1100°C and 1250°C for 72 hrs with average grain sizes of 284 μm and 768 μm respectively.

The twin boundaries observed in Figure 29 (c-f) can be explained as annealing twins formed as a part of recrystallization process during heat treatments. The model that explains this phenomenon is growth accident model.[17][18] The growth accident model states that a coherent twin boundary forms at a migrating grain boundary due to a stacking error. This model is widely used to explain twin formation during heat treatments. The amount of driving force acting on grain boundary migration and the resulting migration velocity are considered to be the promoting factors for the generation of annealing twins by the growth accident model.[19][18]

4.2 FeNiCrCoAl high entropy alloy

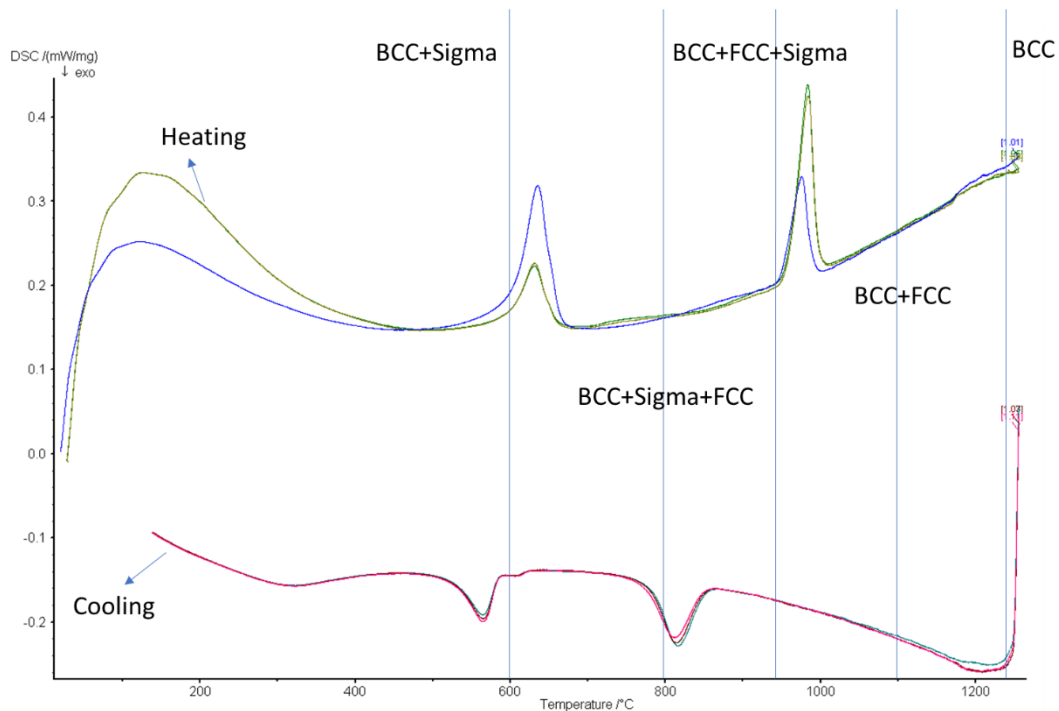


Figure 30 Differential calorimeter plot for as cast FeNiCrCoAl HEA for the temperature range 200°C – 1250°C. The phases present obtained from XRD analysis are indicated at the respective temperature values

Figure 30, shows the differential scanning calorimeter (DSC) trace for FeNiCrCoAl high entropy alloy system, containing two reversible peaks suggesting a phase change in the alloy system during the heat cycle of the experiment. We observe that the DSC trace coincides with the XRD results, showing peak formation for the phase transformation as a function of temperature. Using TCFE8 database for prediction of phases in Thermo-Calc, we observe phase transformation only around 600°C. Using SSOL2 database and TTNI6 database, we observe phase transformations for temperature range of 600°C to 1250°C which coincides well with the DSC trace shown in Figure 30.

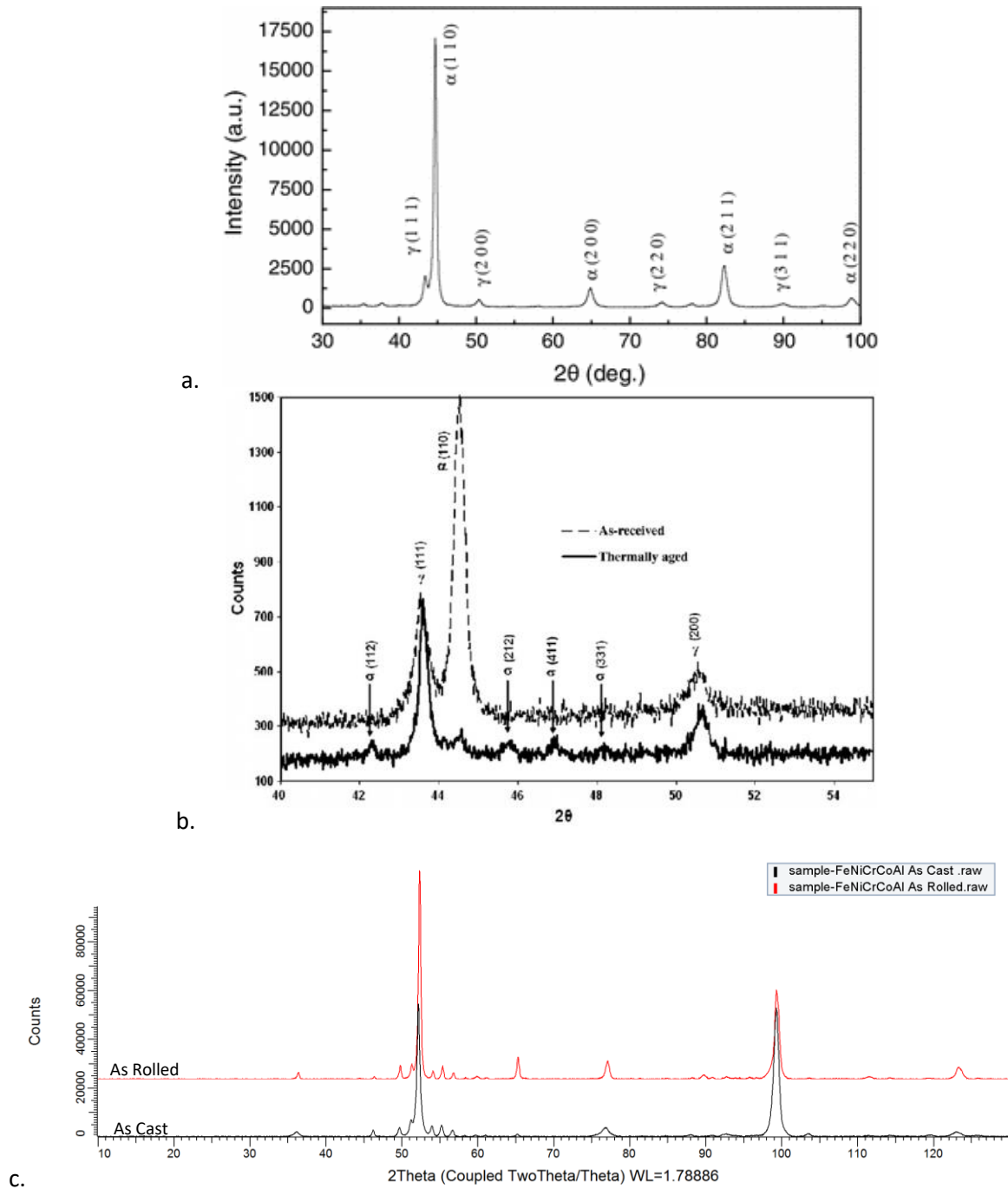


Figure 31 a. XRD plot of Iron system representing the peaks for BCC(α) structure and FCC(γ) structure and the corresponding planes in the system. b. XRD plot of Duplex stainless steel representing the peaks for BCC(α), Sigma(σ) and FCC(γ) phases c. Experimental XRD results depicting phases present in FeNiCrCoAl HEA system for as cast and as rolled samples.

Figure 31(c) shows the XRD patterns of FeNiCrCoAl high entropy alloy system for both as cast and as rolled starting conditions. For both conditions, the alloy is a two-phase system consisting of BCC and Sigma phases.

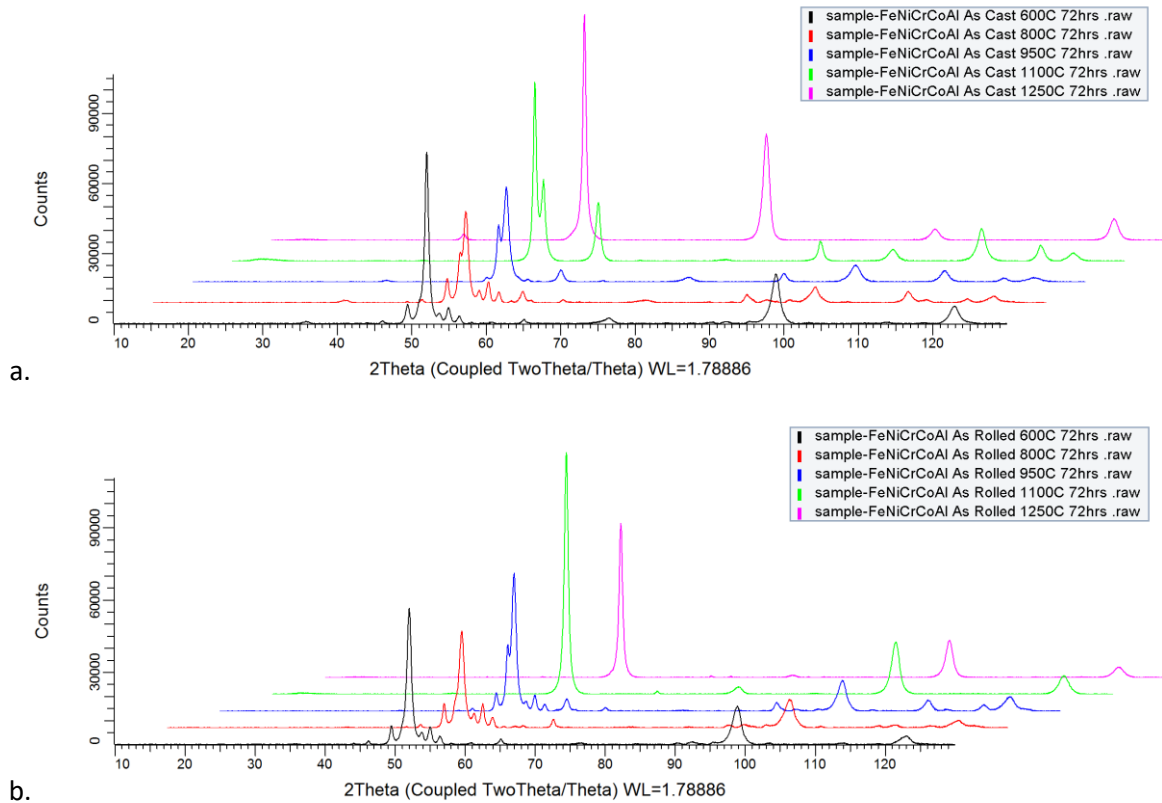


Figure 32 Experimental XRD results depicting phases present in (a) as cast condition samples after heat treatments at different temperatures for 72hrs (b) as rolled condition samples after heat treatments at different temperatures for 72hrs

Figure 32 (a) shows the evolution of phases as a function of temperature from the phases present in the as cast condition of the material. BCC and sigma phases present in the as cast condition of the material are also present in the material after 600°C heat treatment for 72 hrs. FCC phase forms in the material and the material becomes a three-phase system with BCC, sigma and FCC phases after 800°C heat treatment for 72 hrs. After the heat treatment at 950°C for 72 hrs, the material changes into a two-phase system with BCC and FCC phases from a two-phase system of BCC and sigma observed for as cast condition in Figure 31. This holds true for the material after the heat treatment at 1100°C for 72 hrs and the texture becomes strong for the FCC phase when compared to the material after heat treatment for 900°C. The material changes to a single-phase BCC system after the heat treatment at 1250°C for 72 hrs.

Figure 32 (b) shows the phase evolution in the samples for as rolled starting condition for different heat treatments. The phases in the sample from as rolled condition (BCC and sigma) continue to exist in the samples even after heat treatments at 600°C and 800°C for 72hrs. After 950°C heat treatment for 72hrs, the sample becomes a three-phase system with the formation of FCC phase in the sample. The samples become a single-phase BCC system after heat treatments at 1100°C and 1250°C for 72hrs.

Phase fractions of every microstructural constituent in the system obtained at each temperature can also be calculated using XRD measurements. The results are given in Table 6.

Table 6 Phase fractions present in the as cast FeNiCrCoAl for different heat treatments obtained from XRD analysis

FeNiCrCoAl as cast condition			
Temperature	Phase fractions		
	BCC	Sigma	FCC
Un treated	77	23	0
600°C	64	36	0
800°C	41	21	38
950°C	63	0	37
1100°C	31	0	69
1250°C	100	0	0

These values mostly correspond well with the Thermo-Calc predictions. For instance, the phase fraction of BCC obtained using XRD is similar to the sum of the phase fractions of BCC variants predicted by Thermo-Calc. The only deviation between the Thermo-Calc and XRD results is seen at 1100°C heat treatment. This deviation could be explained by the influence of texture on the intensity of FCC peak, affecting the calculation of phase fraction using XRD measurements.

From Figure 31 and Figure 32, we observe that the BCC phase is the dominant phase in the material for both the starting conditions of the alloy and after heat treatments are carried out. Sigma and FCC phases can be considered as secondary or intermediate phases that form at certain temperatures and dissolve into the matrix at higher temperatures, changing the system to a single-phase BCC system. Comparing the results from XRD, DSC and Thermo-Calc predictions, TTNI6 database provides closest predictions to the experimental values and could be considered as a reference database for the FeNiCrCoAl high entropy alloy studied in this report.

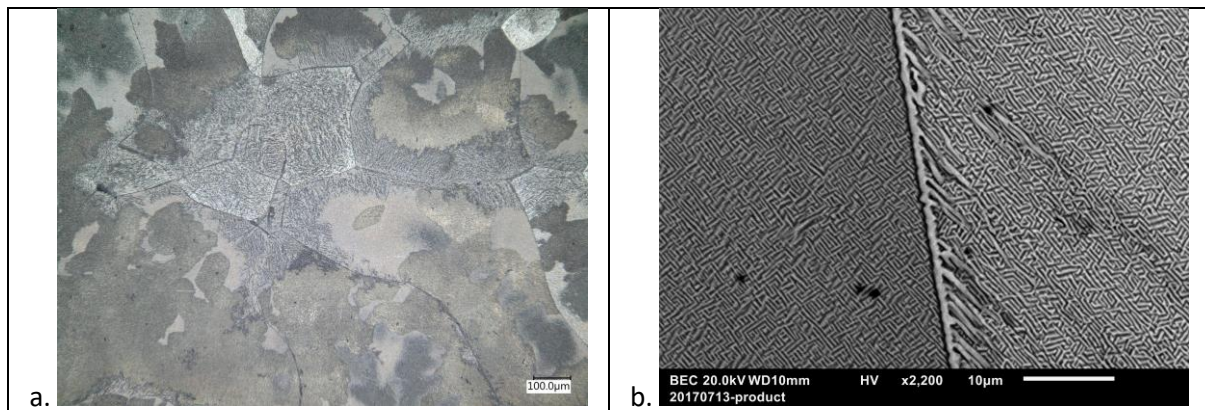


Figure 33 a. Optical micrograph of etched as cast FeNiCrCoAl HEA b. Backscattered electron image of as cast FeNiCrCoAl HEA showing a grain boundary

As observed in Figure 31, FeNiCrCoAl high entropy alloy consists of a two-phase system, BCC and sigma phase, for both as cast and as rolled conditions. Figure 33 (a, b), shows the microstructure of the as cast FeNiCrCoAl high entropy alloy. Etched micrograph shows two distinct regions (dark and bright) suggesting the presence of two phases in the system. Back scattered electron images at higher magnification show a maze-like structure embedded in the matrix. Further analysis on elemental distribution and phase determination, Energy dispersive spectroscopy (EDS) was carried out.

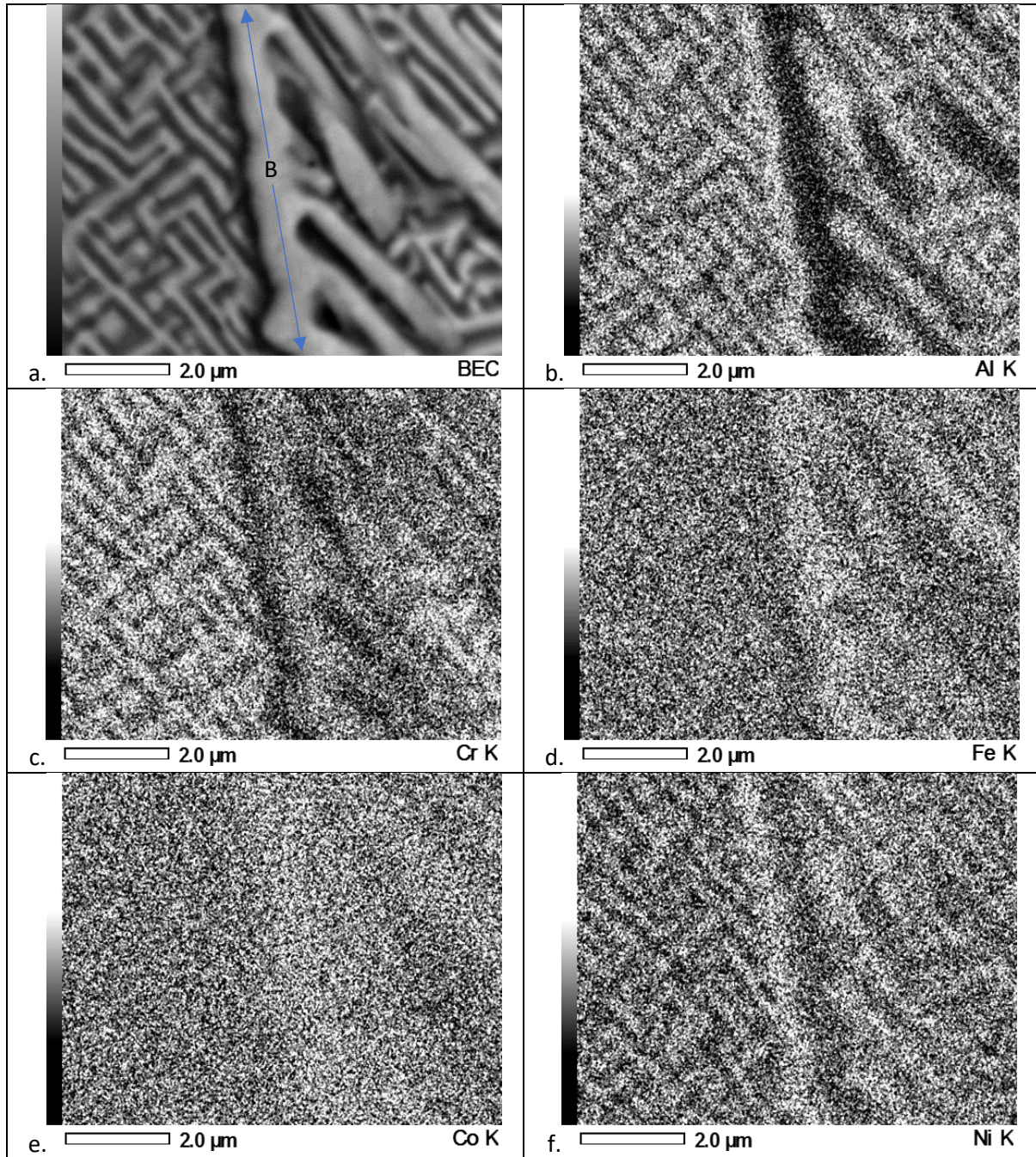


Figure 34 Elemental mapping done near a grain boundary in FeNiCrCoAl as cast HEA with Energy dispersive spectroscopy (EDS). The area marked as B represents grain boundary. (Grey scale is used to show the segregation of elements and could not be quantified. Brighter the region, higher the fraction of the element detected and vice versa)

Figure 34(a) shows the region selected to perform EDS analysis in as cast FeNiCrCoAl high entropy alloy. Figure 34(b-f) show the elemental maps of Al-, Cr-, Fe-, Co- and Ni- respectively. We can observe that the distribution of elements Al and Ni follow a similar trend and are present in the dark regions between the ridges seen in the microstructure. The ridges seen in the matrix are enriched in Cr. The grain boundary is enriched in Fe and a certain fraction of Cr is also seen. There is no significant segregation of Co and Fe in the matrix.

From Figure 24(c), we have seen the possible phases for this alloy system. As discussed earlier, Al does not form a sigma phase. Based on that discussion, the areas enriched in other elements such as Cr and Fe can be considered as sigma phase. The areas enriched in Al can be considered as BCC phase. The

width of the grain boundary is in the order of $0.7\ \mu\text{m}$ and is enriched in Fe and Cr. This suggests the nucleation of sigma phase at the grain boundaries and the branches extending into the matrix suggest the growth of sigma phase from the boundary into the matrix. Thus, with the combination of results from Thermo-Calc, XRD, BSE image and EDS analysis, we can confirm the presence of two phases in the as cast FeNiCrCoAl alloy.

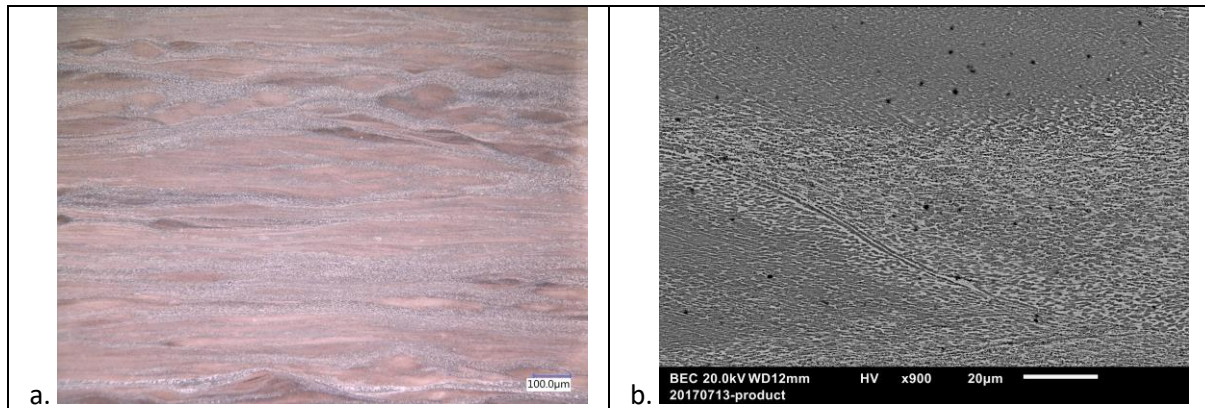
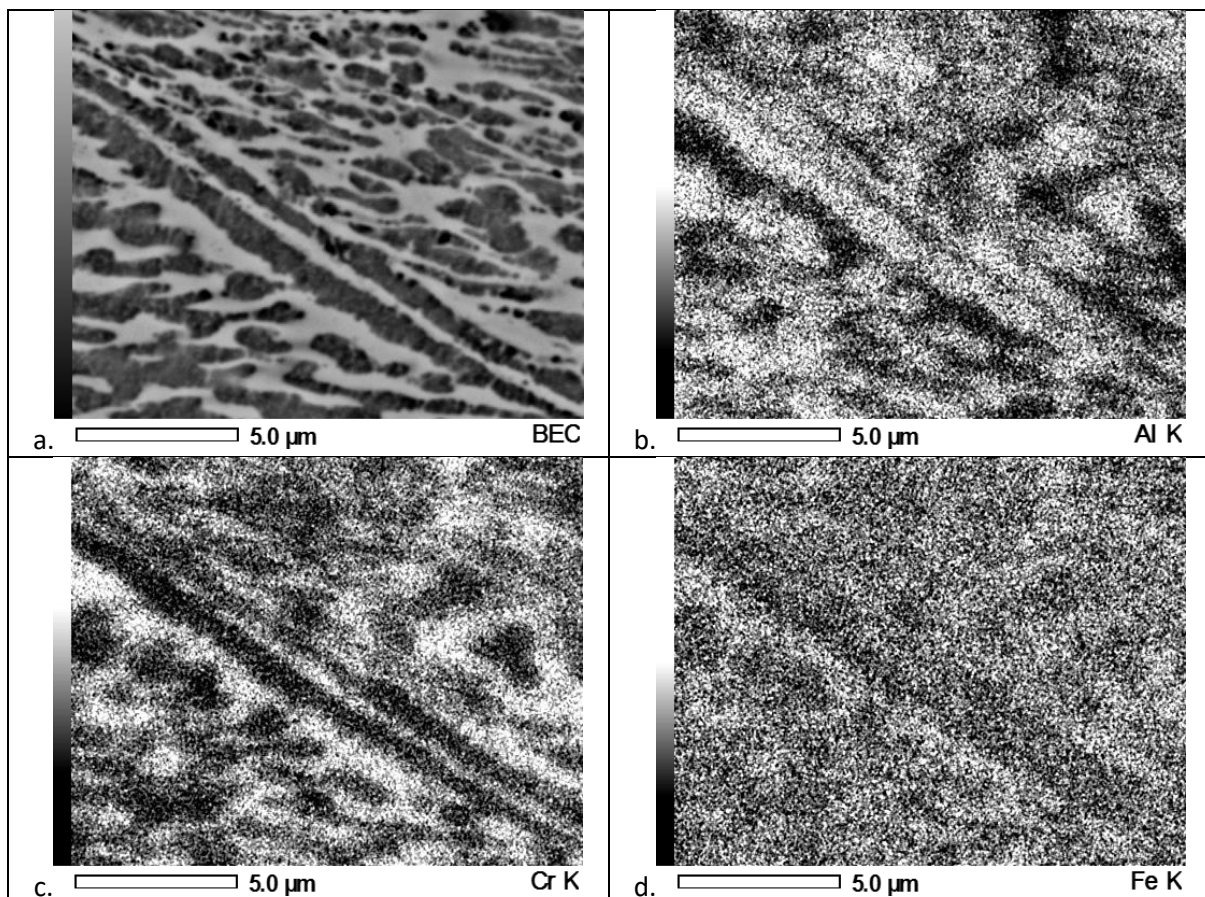


Figure 35 a. Optical micrograph of etched as rolled FeNiCrCoAl HEA b. Backscattered electron image of as rolled FeNiCrCoAl HEA

Figure 35 shows the etched optical micrograph and back scattered electron image of as rolled FeNiCrCoAl high entropy alloy revealing the microstructure. It is observed that the microstructure of the as cast system shown in Figure 33 is distorted during the rolling process resulting in the deformation bands containing two regions (dark and bright).



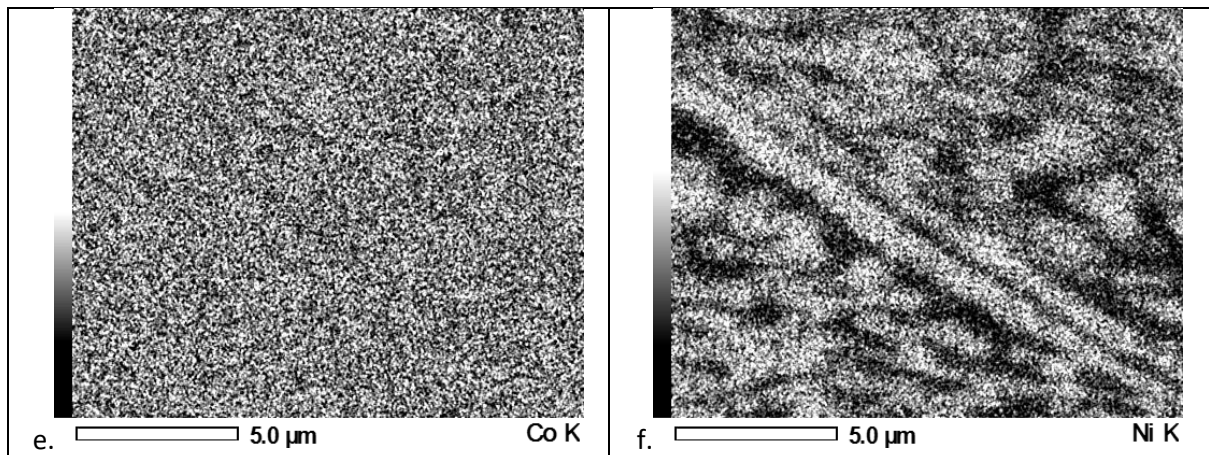
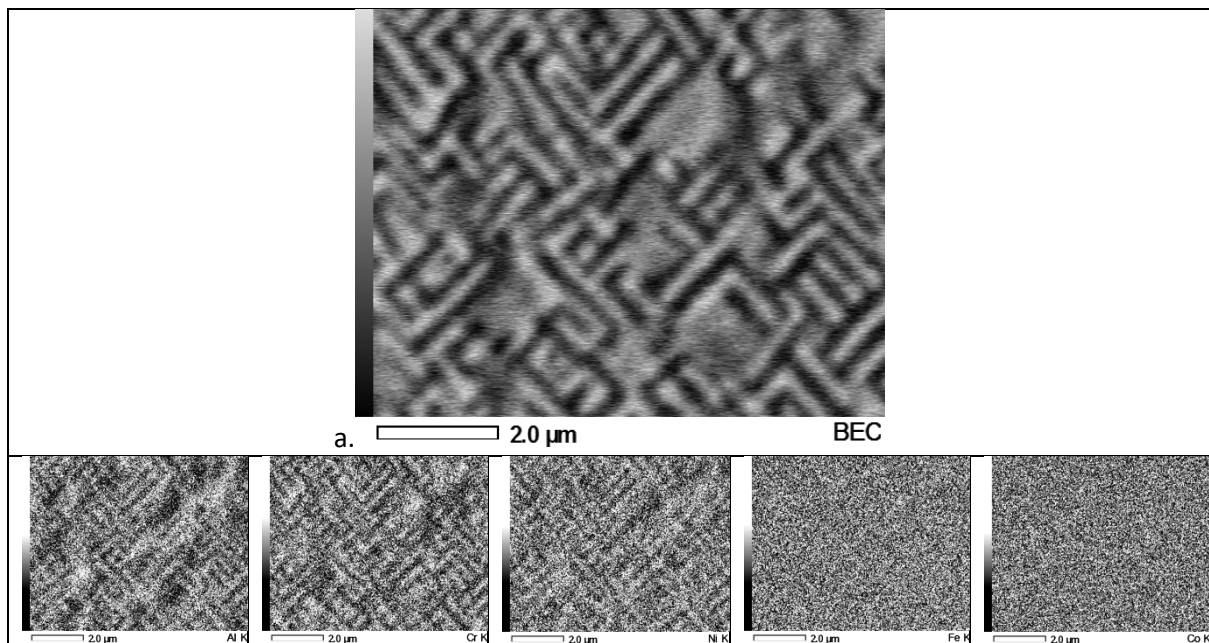


Figure 36 Elemental mapping done on a selected area of FeNiCrCoAl as rolled HEA using Energy dispersive spectroscopy (EDS)

The dark regions seen in the BSE image shown in Figure 36, are enriched in Al- and Ni- while the bright regions are enriched with Cr- along with Fe- enrichment to a little extent. There is no significant segregation of Co- in the observed area of the system. As discussed for the as cast sample, the same can be applied to the as rolled condition as the segregation behaviour is similar for both conditions. The dark regions enriched in Ni- and Al- is can be considered as BCC and the bright regions enriched in Cr- and Fe- can be considered as Sigma phase. With the combination of XRD, optical and BSE images we can conclude the presence of two phases, BCC and sigma, for the as rolled condition of the alloy.



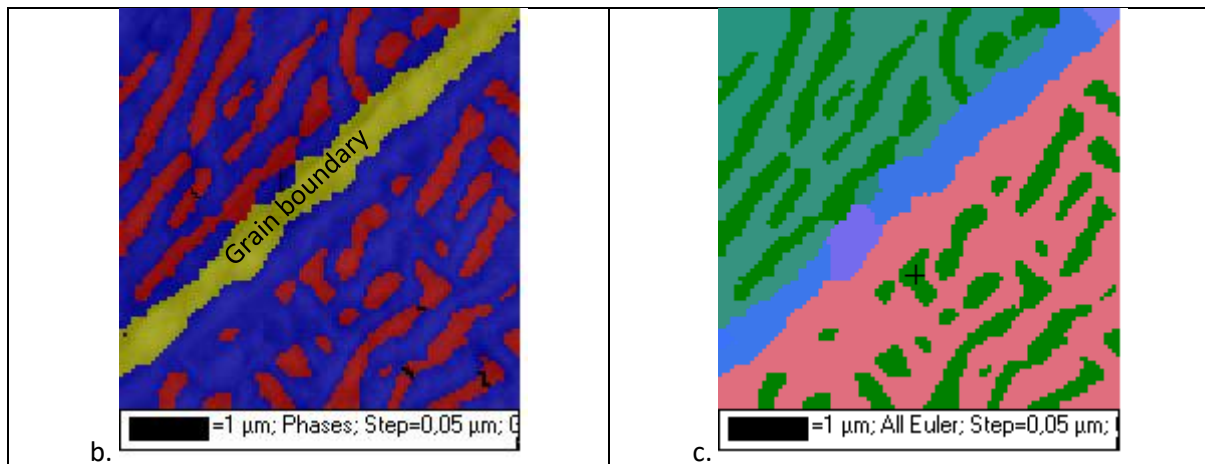


Figure 37 Sample: as cast FeNiCrCoAl HEA after 600°C heat treatment for 72hrs a. followed by elemental maps showing the concentration of elements over the selected area of the sample. b. Image showing the different phases present in the sample obtained using electron back scattered diffraction technique (EBSD), {Red=Sigma phase, Blue=BCC phase and Yellow=FCC phase} (c) Image showing orientation map of the sample.

Figure 37 (a) shows a maze-like structure embedded in the matrix of the as cast FeNiCrCoAl sample heat treated at 600°C for 72hrs as observed in the as cast condition sample shown in Figure 35. The EDS analysis done to determine the elemental segregation in the sample after heat treatment are given in Figure 37(a). The ridges of the maze structure are enriched in Cr and the dark regions in between the ridges are enriched in Ni and Al. There is no clear segregation observed for Fe and Co in the sample. Based on the argument used to determine the phases in the as cast sample and the XRD pattern as shown in Figure 32 for this heat treatment condition, we can conclude that the regions enriched in Ni and Al form the BCC phase and the regions with Cr enrichment is sigma phase.

Figure 37(b) shows the image analysed using EBSD technique for the as cast condition sample heat treated at 600°C for 72hrs. The analysis was made near a grain boundary. The image shows the phases present in the sample at the selected area. The red colour represents sigma phase, the blue colour represents BCC phase and the yellow colour represents the FCC phase. The predictions from Thermo-Calc and experimental results from XRD suggests the presence of two phases (BCC and Sigma) in the system for 600°C heat treatment. But, after analysing the sample using EBSD technique, we find the presence of a third phase, FCC in the system. As can be seen in the EBSD image, the FCC phase is present only on the grain boundary which suggests that the nucleation of the phase has taken place during the heat treatment but was unable to get detected using XRD technique due to the low volume interaction. This result fits well with the Thermo-Calc prediction made using TTNi6 database. From the Thermo-Calc, XRD, EDS and EBSD results combined, we can conclude that the two-phase system from as cast condition changes to a three-phase system with BCC, Sigma and FCC phases after 600°C heat treatment for 72hrs.

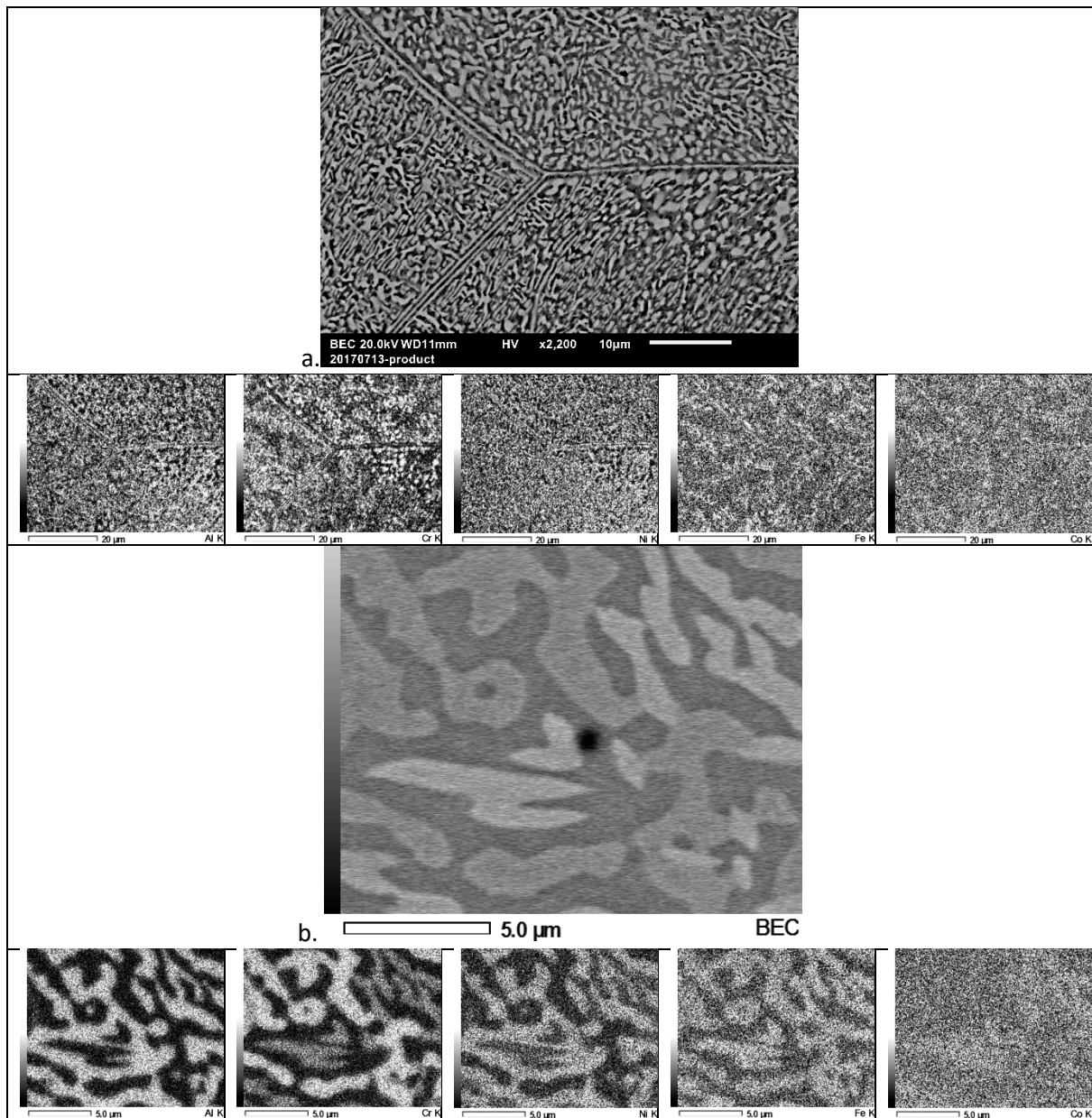


Figure 38 Back scattered electron image of (a) 800°C for 72hrs heat treated as cast FeNiCrCoAl HEA, followed by elemental maps showing the concentration of elements over the selected area of the sample (b) 950°C for 72hrs heat treated as cast FeNiCrCoAl HEA, followed by elemental maps showing the concentration of elements over the selected area of the sample

Figure 38(a) shows the backscattered electron (BSE) image at a triple grain boundary in the as cast sample after 800°C heat treatment for 72hrs. The elemental maps obtained from EDS analysis show the segregation of elements in the sample. From the elemental maps, it can be observed that there are three segregation regions with different sets of elements. One region is enriched in Ni and Al, second region is enriched in Cr and the third region is enriched in Fe along with enrichment of Co and Ni to a certain extent. Based on the phases identified from XRD analysis, Thermo-Calc predictions of phases and phase constitutions and EDS analysis, we can conclude that the regions with Ni and Al enrichment form BCC phase, regions with Cr enrichment form Sigma phase and the regions enriched in Fe, Co and Ni form FCC phase, making the sample a three-phase system after 800°C heat treatment after 72hrs.

Figure 38(b) shows the BSE image of the as cast sample heat treated at 950°C for 72hrs along with the elemental maps showing the segregation of elements obtained from EDS technique. In the elemental

maps, we observe a clear segregation of elements in to three regions, regions enriched in Ni and Al, regions enriched in Cr with a small fraction of Fe enrichment, regions enriched in Fe with small enrichment of Ni, Cr and Co. Apart from the regions with Fe enrichment, there is no clear segregation of Co in the sample.

The sample after 950°C heat treatment follows the same segregation behaviour of elements as observed in the sample after 800°C heat treatment but the segregation of elements is more pronounced in the sample after 950°C heat treatment. Comparing the internal morphology of the grain between the samples after 800°C and 950°C heat treatments, we observe the coarsening of the regions. Thus, for the as cast sample after heat treatment at 950°C for 72hrs, we observe three regions with different elemental segregations and can conclude the existence of three phases in the system (BCC, Sigma and FCC).

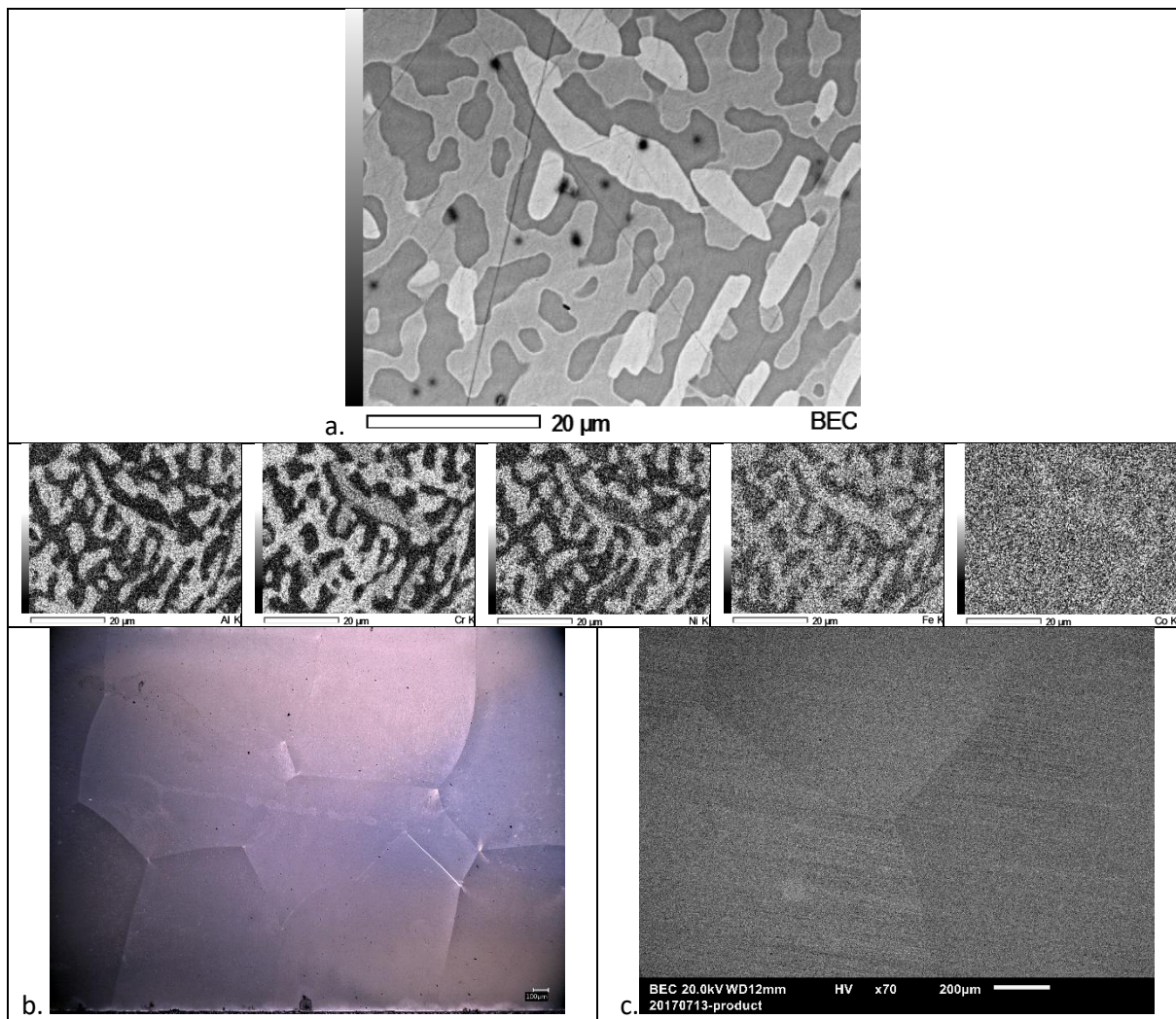


Figure 39 a. Backscattered image of 1100°C for 72hrs heat treated as cast FeNiCrCoAl HEA, followed by elemental maps showing the concentration of elements over the selected area of the sample. b. optical micrograph of etched FeNiCrCoAl HEA after 1250°C heat treatment for 72hrs c. Back scattered electron image of FeNiCrCoAl HEA after 1250°C heat treatment for 72 hrs

Figure 39(a) shows the BEC image of the as cast sample after 1100°C heat treatment for 72 hrs, followed by elemental maps obtained using EDS technique. The segregation of elements in the sample follows the similar trend observed in the as cast samples after heat treatments at 800°C and 950°C for 72hrs as shown in Figure 38. The region with Ni and Al enrichment (dark grey region), region with Cr enrichment along with a certain fraction of Fe enrichment (light grey region) and the regions with Fe

enrichment with a certain fraction of Ni, Co and Cr enrichment (bright region). The segregation of Co is not significant in the rest of the sample. As pointed out earlier, XRD results and Thermo-Calc predictions show that the heat treatment at 1100°C would lead to a two-phase system with BCC and FCC. Furthermore, it was also mentioned that regions enriched with Ni and Al would be a BCC phase. Additionally, thermodynamic predictions of binary Fe-Cr system suggest that the sigma phase decomposes into a BCC phase above 830°C. This correlates well with the EDS measurements in Figure 39 (a) where two variants of BCC with different chemical compositions is present (light gray + dark grey regions). This also corresponds well with the Thermo-Calc predictions which shows two variants of BCC. Phase fraction analysis based in EDS map shows that BCC fraction (light grey + dark grey) is higher than the FCC fraction (bright region). Further analysis is performed using EBSD technique to determine the phases present in the system as shown in Figure 40.

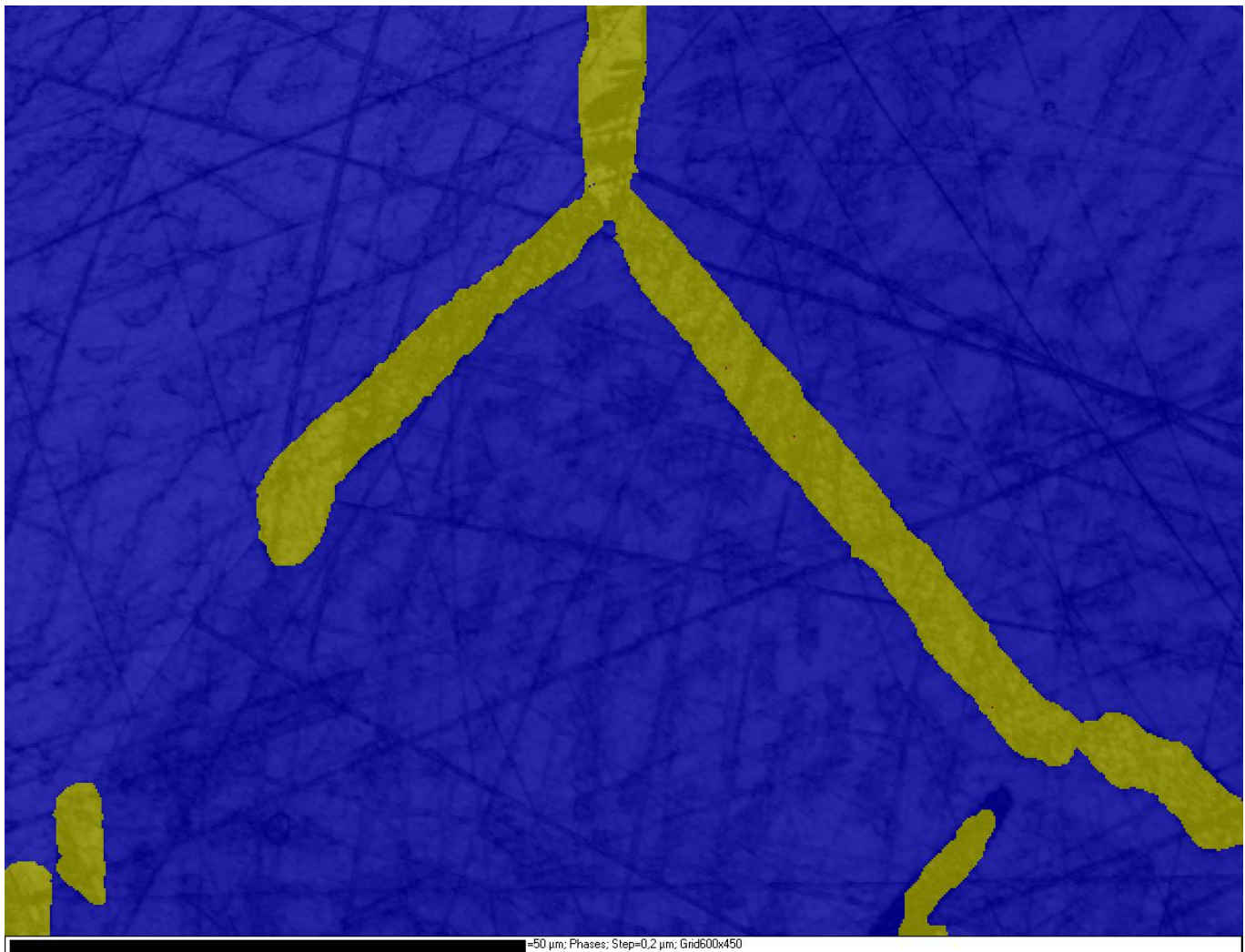


Figure 40 EBSD analysis image of the as cast FeNiCrCoAl HEA after heat treatment at 1100°C for 72hrs {Blue=BCC phase, Yellow= FCC phase}

As observed in Figure 40, EBSD technique identifies only BCC and FCC phases present in the sample with no sigma phase identified. The EBSD analysis was performed with the XRD data as reference which contains only one set of parameters for BCC phase. Thus, we do not observe identification of different variants of BCC in EBSD analysis. With the EBSD data along with XRD results we can conclude the material is changed to a two-phase system with BCC (two variants with different compositions) and FCC after 1100°C heat treatment from the as cast material containing BCC and Sigma phases.

Similar to EDS analysis, EBSD data also shows that BCC fraction (Blue) is higher than FCC fraction (yellow). These results are in line with the Thermo-Calc predictions given in Table 5.

Figure 39 (b) and (c) show the optical micrograph and BSE image of the as cast sample after heat treatment at 1250°C for 72hrs. There is no internal morphology and significant segregation of elements observed inside the grains as seen in the as cast samples for lower temperature heat treatments from both optical and BSE images of the sample. XRD results and Thermo-Calc predictions both present a single-phase BCC structure for the 1250°C heat treatment. Thus, we can conclude that the as cast sample with two phases, BCC and sigma becomes a single-phase BCC system after heat treatment at 1250°C for 72hrs.

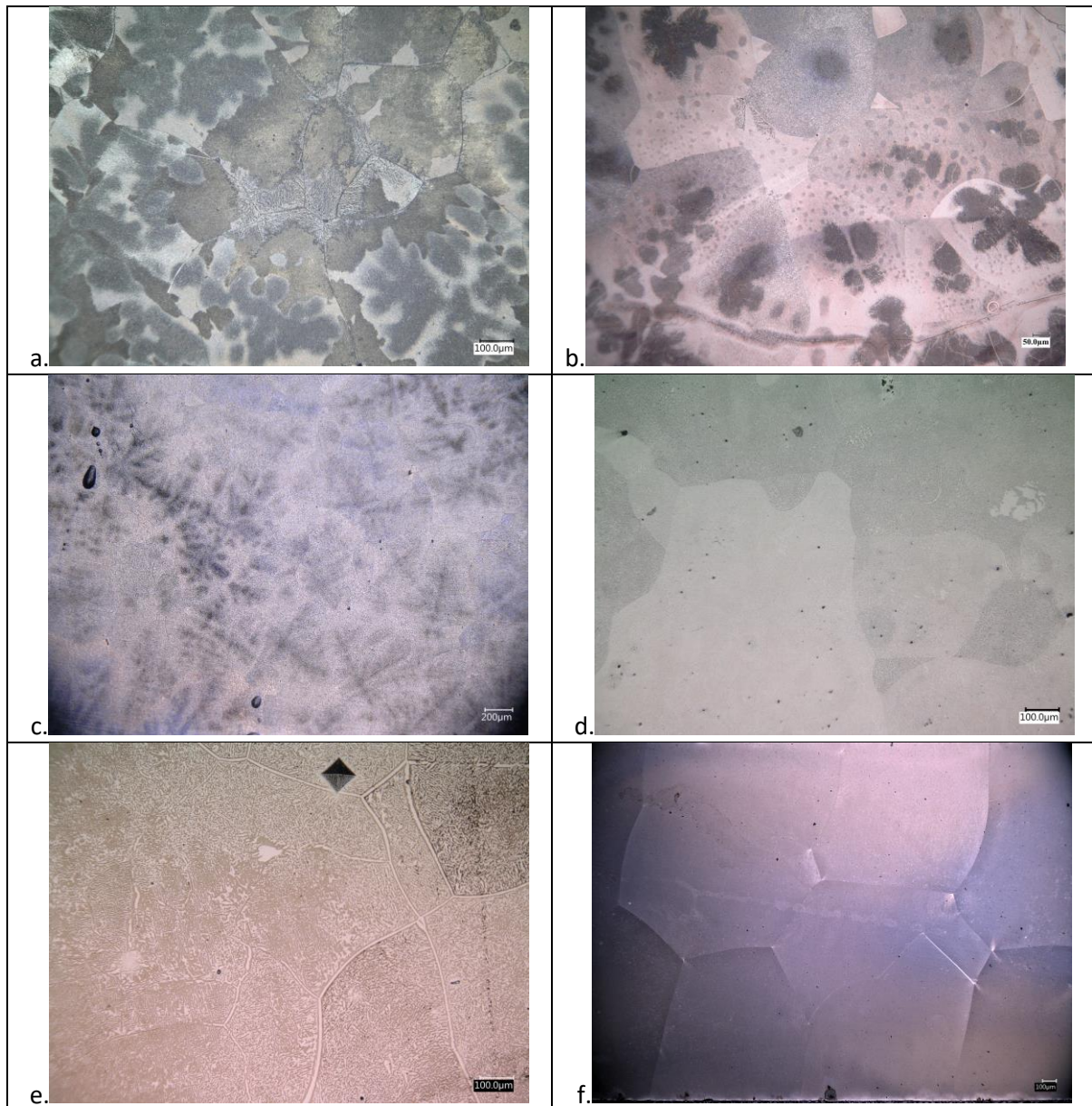


Figure 41 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy and for different heat treated conditions for 72hrs a. as cast sample b. 600°C c. 800°C d. 950°C e. 1100°C f. 1250°C (The difference in appearance is due to the different due to different immersion times during etching process and also could be due to etchant itself)

Figure 41 shows the evolution of microstructure of FeNiCrCoAl high entropy alloy from as cast condition to heat treatments at 600°C, 800°C, 950°C, 1100°C and 1250°C. The as cast microstructure

shown in Figure 41(a) contains grains enclosing dendritic structures. The average grain size is 400 μm . The volume fraction of the dendrite structures reduces after 600°C heat treatment for 72 hrs and reduces further after the heat treatment at 800°C for 72 hrs as observed in Figure 41(b) and (c). The average grain sizes after 600°C and 800°C heat treatment are 435 μm and 480 μm . The dendritic structures dissolve completely in the matrix after the heat treatment at 950°C for 72 hrs. The average grain size in the sample is 480 μm . After the heat treatment at 1100°C for 72hrs, the average grain size in the sample is still 480 μm . The internal morphology of the grains is more clearly visible in the optical micrograph due to coarsening as observed in BSE images shown in Figure 33, Figure 37 and Figure 38. The sample does not show any internal morphology as observed in samples for lower temperature heat treatments and exhibits significant grain growth after heat treatment at 1250°C for 72 hrs. The average grain size in the sample is 1370 μm (1.37 mm). We will discuss the effect of different phases and grain sizes on the mechanical behaviour in the later sections of this report.

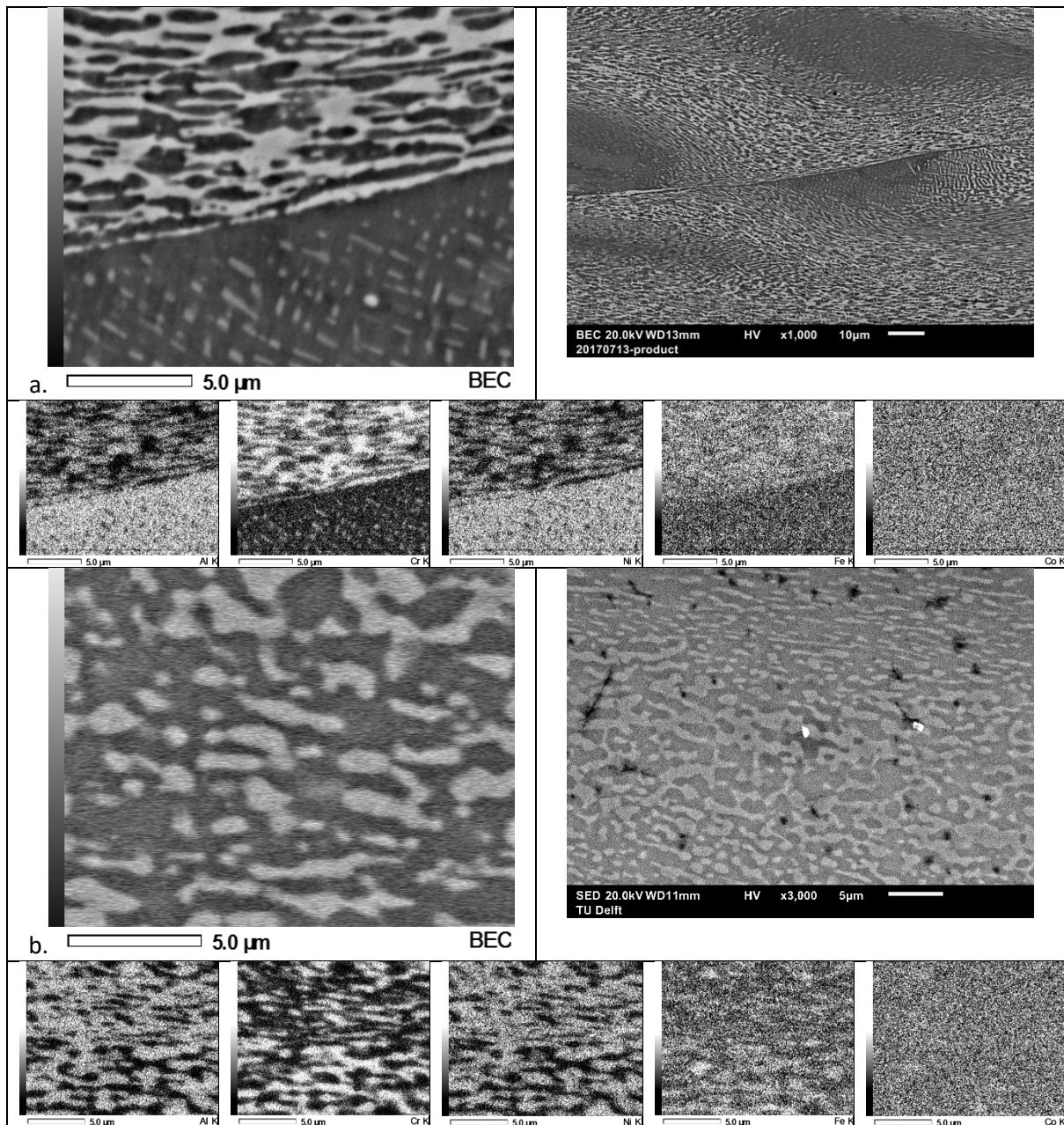
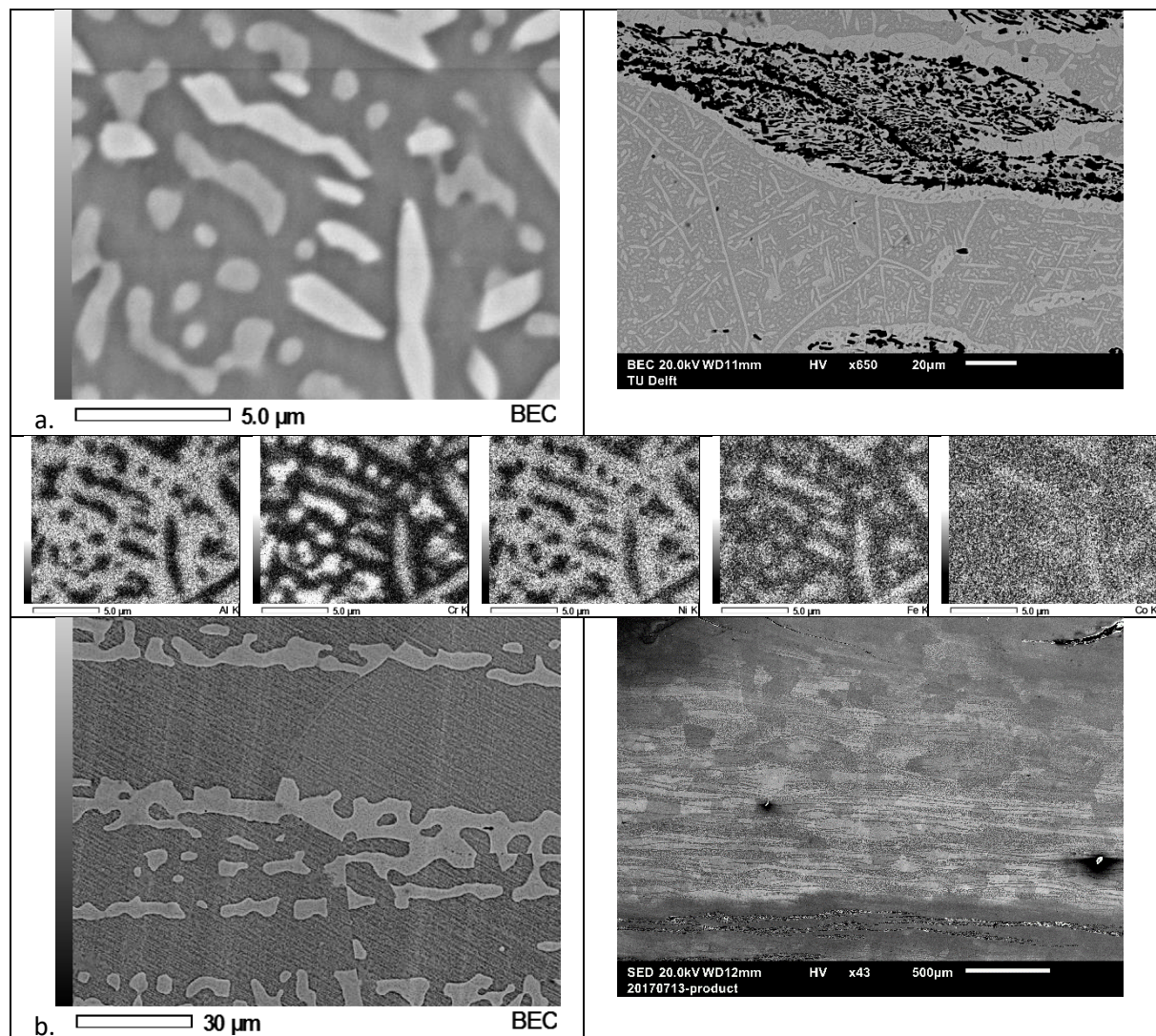


Figure 42 Back scattered electron image of (a) 600°C for 72hrs heat treated as rolled FeNiCrCoAl HEA, followed by elemental maps showing the concentration of elements over the selected area of the sample (b) 800°C for 72hrs heat treated as rolled FeNiCrCoAl HEA, followed by elemental maps showing the concentration of elements over the selected area of the sample

Figure 42 (a) shows the microstructure of the as rolled FeNiCrCoAl HEA after 600°C heat treatment for 72 hrs. The low magnification BSE image shows the existence of rolled microstructure even after the heat treatment. We observe dark and bright regions in the microstructure and EDS analysis was carried out to determine the segregation of elements in the material. The elemental maps show a similar trend in segregation of Ni and Al which suggests the presence of BCC phase as discussed for the as cast condition. The bright regions are enriched in Cr and Fe suggesting the presence of sigma phase. There is no significant segregation observed for Co in the sample.

Figure 42 (b) shows the microstructure of the as rolled FeNiCrCoAl HEA after 800°C heat treatment for 72 hrs. The elemental maps suggest that the dark regions in the material are enriched in Ni and Al suggesting BCC phase. The bright regions are enriched in Cr with a small fraction of enrichment in Fe suggesting sigma phase. There are also some regions with Fe enrichment with a small fraction of enrichment in Ni and Cr. This is the same condition as observed in Figure 37 for as cast FeNiCrCoAl after heat treatment at 600°C for 72 hrs. The same explanation could be used here to suggest the presence of a third phase (FCC) in the system by comparing the trends followed in the elemental segregation maps. We do not get the identification for FCC phase in XRD analysis and that could be due to the small interaction volume of the FCC phase in the material.



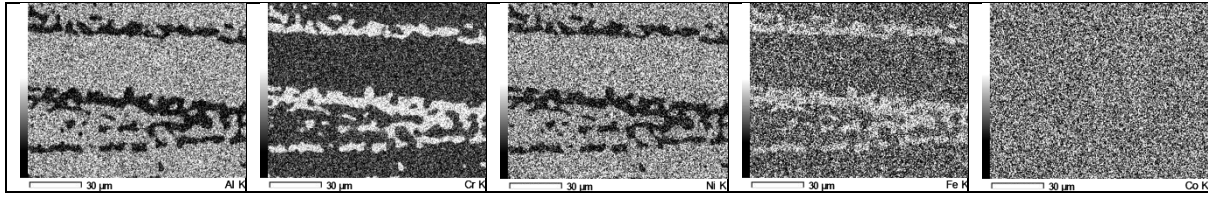


Figure 43 Back scattered electron image of a. 950°C for 72hrs heat treated as rolled FeNiCrCoAl HEA followed by elemental maps showing the concentration of elements over the selected area of the sample b. 1100°C for 72hrs heat treated as rolled FeNiCrCoAl HEA followed by elemental maps showing the concentration of elements over the selected area of the sample

Figure 43 (a) shows the selected area of interest to perform the EDS analysis along with the low magnification BSE image of the sample after heat treatment at 950°C for 72 hrs. The elemental maps show the segregation of the elements in the material. From the phases and their constitutions predicted by Thermo-Calc and experimental XRD results obtained for this sample, the regions enriched in Ni and Al suggest BCC phase, the regions enriched in Cr along with a small fraction of enrichment in Fe suggests sigma phase and the regions enriched in Fe along with small fraction of enrichment in Cr and Ni suggests FCC phase in the material. The two-phase (BCC and Sigma) changes to a three-phase system with the nucleation and growth of FCC phase during the 950°C heat treatment for 72 hrs. From the low magnification BSE image, we observe the partial recrystallization and growth that took place in the material during the heat treatment. The grain size in the sample is in the order of 40 µm.

Figure 43 (b) shows the selected area of interest in the sample after 1100°C heat treatment for 72 hrs along with the low magnification BSE image and the elemental maps showing the segregation of elements in the material. There are two regions in the material, dark regions enriched in Ni and Al and the bright regions enriched in Cr and small fraction of enrichment in Fe. There is no significant segregation observed for Co in the whole area selected for analysis and Fe in the dark regions.

XRD analysis from Figure 32 shows that the sample after 1100°C heat treatment for 72 hrs becomes a single-phase BCC structured system. Thermo-Calc predictions as seen in Figure 24 show BCC_B2 and BCC_A2 as possible phases. Comparing these results (XRD, Thermo-Calc and EDS), we can conclude that the sample becomes a single-phase BCC system after 1100°C heat treatment for 72 hrs.

From the low magnification BSE image, we observe that partial recrystallization and grain growth occurred in the sample during the heat treatment with the grain size in the order of 100 µm.

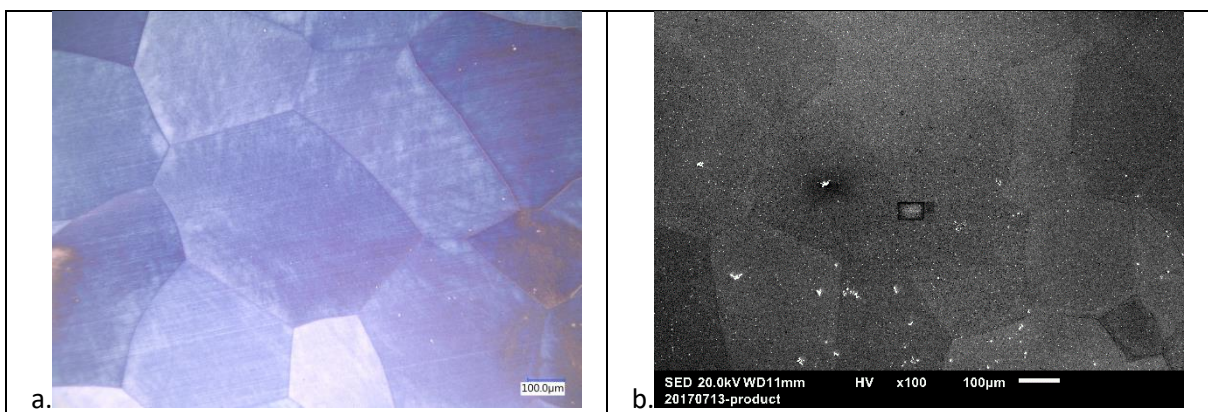


Figure 44 a. optical micrograph of etched as rolled FeNiCrCoAl HEA b. Back scattered electron image of as rolled FeNiCrCoAl HEA after 1250°C heat treatment for 72 hrs

Figure 44 shows the etched optical micrograph and BSE image of as rolled FeNiCrCoAl HEA after 1250°C heat treatment for 72 hrs. We observe full recrystallization and grain growth in the sample. There is no internal morphology observed in the material as seen in previous microstructures of the material underwent lower temperature heat treatment processes or any elemental segregation in the

material. XRD results along with optical and SEM results show a single-phase BCC structure in the system. The optical micrograph and BSE image show equiaxed grains with the average grain of 610 μm .

In summary, FeNiCrCo high entropy alloy is a single phase FCC system for all thermo-mechanical treatments that are applied in this study where as FeNiCrCoAl high entropy alloy starts with a two phase system (BCC+sigma) for the as cast and as rolled conditions. The as cast FeNiCrCoAl alloy contains three phases (BCC+sigma+FCC) for the temperatures 600°C, 800°C and 950°C and the as rolled material contains three phases (BCC+sigma+FCC) only at 950°C. The as cast FeNiCrCoAl alloy becomes a two-phase system (BCC+FCC) after 1100°C heat treatment where in as rolled material is observed to become a single-phase BCC system. Both as cast and as rolled condition samples become single-phase BCC systems after 1250°C heat treatment.

This trend in phase formation observed for as cast and as rolled conditions of FeNiCrCoAl high entropy alloy suggests an influence of deformation (in this study, hot rolling) on the phase formation in the alloy.

The as cast microstructure for FeNiCrCo alloy show dendrites along with elongated grains at the edge of the ingot and equiaxed grains towards the center whereas for FeNiCrCoAl alloy, we observe large grains with dendrites. After rolling, we observe full recrystallization after 950°C heat treatment for FeNiCrCo alloy and for FeNiCrCoAl alloy, we observe the same after 1250°C heat treatment. This could be due to the increasing effect of the 'sluggish diffusion' property due to the addition of one element in the FeNiCrCoAl alloy compared to FeNiCrCo alloy.

4.3 Hardness Measurement

In this section, we will discuss the hardness profile of the material after undergoing different thermo-mechanical processing with respect to temperature, phase fractions and grain sizes.

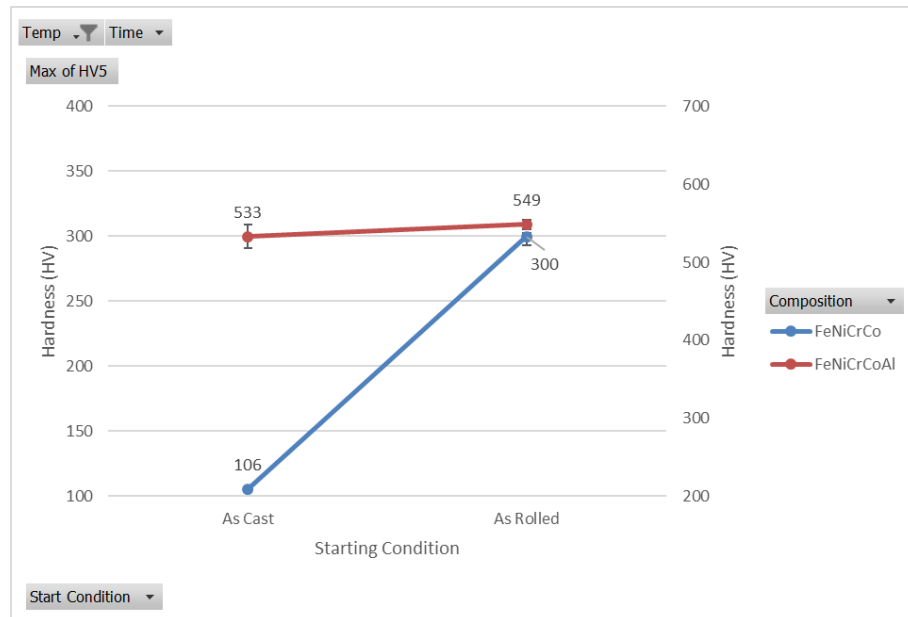


Figure 45 Hardness values of FeNiCrCo and FeNiCrCoAl HEAs for as cast and as rolled starting conditions

Figure 45 shows the hardness values for the starting conditions (as cast and as rolled) of FeNiCrCo and FeNiCrCoAl HEAs. It can be observed that the hardness of these materials increases after the hot rolling process. The hardness of the FeNiCrCo HEA increases significantly (almost three times) after the rolling process whereas the hardness of FeNiCrCoAl HEA increases slightly. From Figure 26, we can observe that the FeNiCrCo alloy for both starting conditions contain FCC phase in the system and from Figure 31, we observe that the FeNiCrCoAl alloy for both starting conditions contain a mixture of BCC and sigma phases in the system.

Assuming the volume fractions of BCC and sigma phases in the as cast or as rolled conditions are directly related to the hardness contribution of the system. using a simple qualitative approach given by,

Total hardness = (volume fraction of BCC x hardness of BCC) + (volume fraction of sigma x hardness of sigma)

the hardness of BCC and sigma phases can be determined. Using the volume fractions obtained by XRD results, the hardness of BCC and sigma phase is calculated to be 579 HV and 379 HV respectively. We observe the hardness of the single-phase BCC system of FeNiCrCoAl is 561 HV. The difference in hardness values could be the change in chemical composition of the BCC phase.

Based on the hardness values obtained, FCC phase has lower hardness value when compared to BCC and sigma phases.

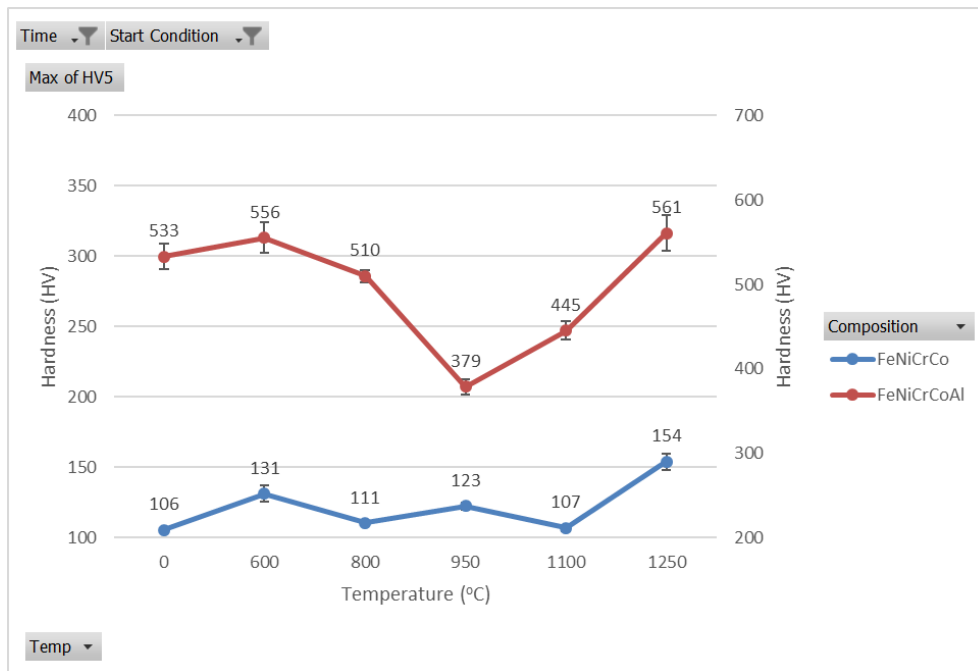


Figure 46 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl HEAs after heat treating at different temperatures for 72hrs

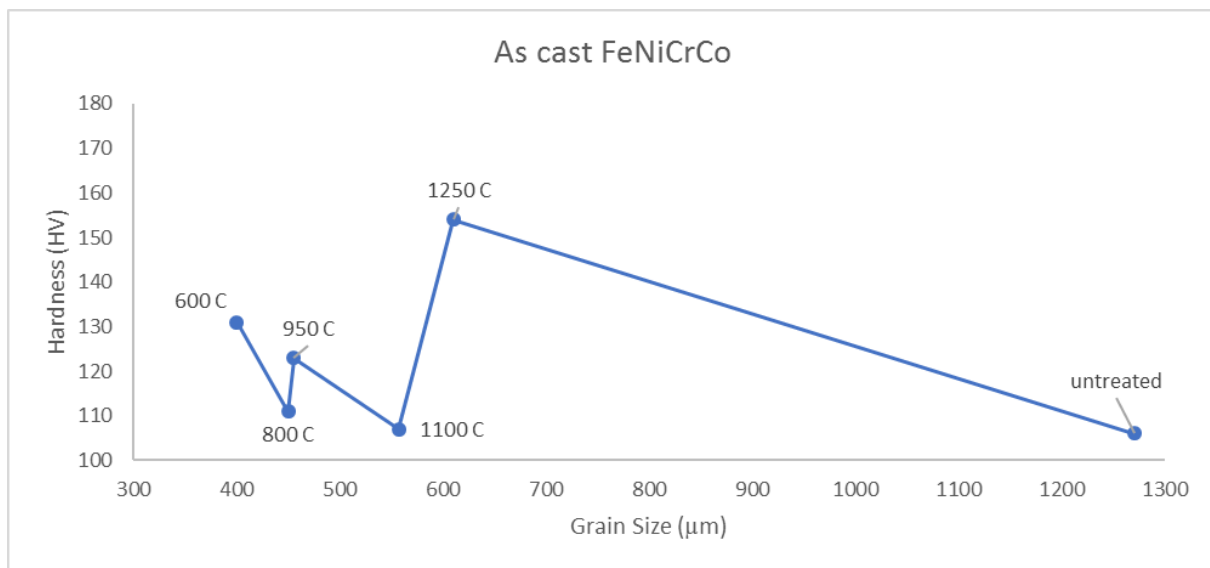


Figure 47 Hardness profile of as cast FeNiCrCo (single-phase FCC system) material with respect to grain sizes after heat treatments and for untreated material

The hardness profile of FeNiCrCo does not follow a monotonous trend with relation to temperature. The increase in hardness after 600°C heat treatment is due to the dissolution of the dendrites into the matrix resulting in more pronounced solid-solution strengthening effect without any segregation of elements as seen for as cast condition of the material. The change in hardness values of the material for the heat treatments at 800°C, 950°C and 1100°C is not significant. But when compared the hardness values with grain size of the materials as seen in Figure 47, we see the similar trend in hardness with respect to grain sizes at these temperatures. We observe that as the grain size increases in the material as a function of temperature, hardness value declines for the temperatures 800°C, 950°C and 1100°C. The hardness value of the material increases after the heat treatment at 1250°C and the grain size of the material also increases. Further analysis is required to explain this behaviour

as we do not observe any changes in both morphology or phase formation after 1250°C heat treatment.

The hardness profile of FeNiCrCoAl high entropy alloy as seen in Figure 46 can be related to phases present and phase fractions in the system. Table 5 shows the phase fractions as predicted by TTNi6 database. The trend shown for hardness values as a function of heat treatment temperature corresponds to the variation in one of the variants of BCC (namely, BCC_A2). Figure 48 indicates that the influence of the BCC phase (sum of both variants) is significant on the hardness.

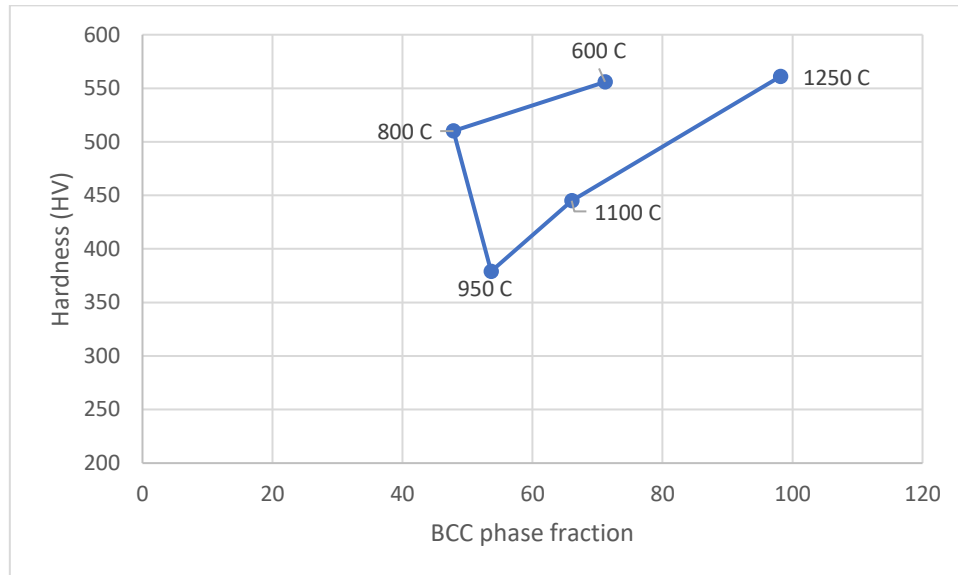


Figure 48 Hardness plot of as cast FeNiCrCoAl vs BCC phase fraction after different heat treatments for temperatures 800°C – 1250°C

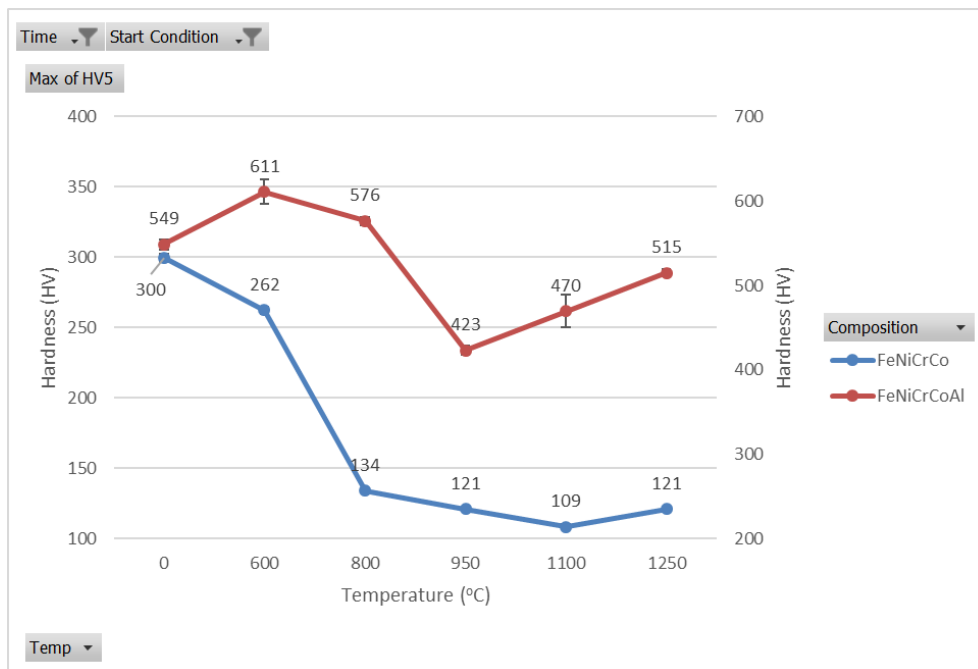


Figure 49 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl HEAs after heat treating at different temperatures for 72hrs

From Figure 49, the hardness profile of as rolled FeNiCrCo high entropy alloy after heat treatments can be explained by the decreasing effect of rolling deformation (stress relaxation) in the material, thermal softening and recrystallization and grain growth as observed in Figure 29. The decrease in the hardness after heat treatment at 600°C is the influence from the initiation of recrystallization in the material. The fraction of recrystallization was calculated to be 45%. Further decrease in hardness value for heat treatment at 800°C is due to increase in recrystallization to 90% accompanied by grain growth. The hardness value change is not significant for the heat treatments at 950°C, 1100°C and 1250°C. The lower hardness value is explained by full recrystallization and grain growth observed in the material as reported in Figure 29.

The hardness profile of the as rolled FeNiCrCoAl high entropy alloy as observed in Figure 49 can be associated with the phase formation, decreasing effect of rolling deformation (stress relaxation), recrystallization and grain growth. The increase in hardness after 600°C heat treatment can be explained by the increase in the sigma phase fraction which is relatively the hard phase in comparison with BCC phase. The decrease in the hardness value after 800°C heat treatment can be explained by the stress relaxation which is observed as the coarsening of microstructure observed in BSE images shown in Figure 42.

The decrease in hardness value after heat treatment at 950°C is due to the formation of relatively soft phase, FCC, in the system accompanied by partial recrystallization. After the 1100°C heat treatment, the system becomes a single-phase BCC system with no influence of relatively soft phases like FCC, thereby increasing the hardness value of the material. The change in hardness from 1100°C heat treatment to 1250°C heat treatment can be explained by the complete dissolution of two variants of BCC with different compositions into a single random BCC solid solution resulting in solid solution strengthening. The phase fractions present in the as rolled FeNiCrCoAl for different heat treatments are tabulated in Table 7.

Table 7 Phase fractions present in the as rolled FeNiCrCoAl for different heat treatments.

FeNiCrCoAl As rolled condition				Hardness (HV)
Temperature	Phase fractions			
	BCC	Sigma	FCC	
Un treated	85	15	0	549
600°C	55	45	0	611
800°C	48	52	0	576
950°C	49	27	24	423
1100°C	100	0	0	470
1250°C	100	0	0	515

5. Conclusion

Based on the results and discussion carried out in the above section, we can conclude that the FeNiCrCo high entropy alloy is a single-phase FCC system for all thermo-mechanical treatments that are applied in this study where as FeNiCrCoAl high entropy alloy starts with a two phase system (BCC+sigma) for the as cast and as rolled conditions. The as cast FeNiCrCoAl alloy contains three phases (BCC+sigma+FCC) for the temperatures 600°C, 800°C and 950°C and the as rolled material contains three phases (BCC+sigma+FCC) only at 950°C. The as cast FeNiCrCoAl alloy becomes a two-phase system (BCC+FCC) after 1100°C heat treatment where in as rolled material is observed to become a single-phase BCC system. Both as cast and as rolled condition samples become single-phase BCC systems after 1250°C heat treatment. The BCC phase consists of two variants with different composition of elements is observed for these temperatures.

This trend in phase formation observed for as cast and as rolled conditions of FeNiCrCoAl high entropy alloy suggests an influence of deformation (in this study, hot rolling) on the phase formation in the alloy.

The as cast microstructure for FeNiCrCo alloy show dendrites along with elongated grains at the edge of the ingot and equiaxed grains towards the center whereas for FeNiCrCoAl alloy, we observe large grains with dendrites. After rolling, we observe full recrystallization after 950°C heat treatment for FeNiCrCo alloy and for FeNiCrCoAl alloy, we observe the same after 1250°C heat treatment. This could be due to the increasing effect of the 'sluggish diffusion' property due to the addition of one element in the FeNiCrCoAl alloy compared to FeNiCrCo alloy.

The hardness of the FeNiCrCoAl follows the trend relatable to the phases present in the material especially the BCC phase variants. The hardness of both the alloy systems doesn't show much dependence on the grain sizes observed in the optical micrographs.

As it is observed from the results that these High entropy alloys have unique behaviour and are to be studied extensively to fully understand their underlying mechanisms. These alloys have great potential to replace the existing materials in the field of structural, nuclear, aerospace and aviation applications.

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Appendix

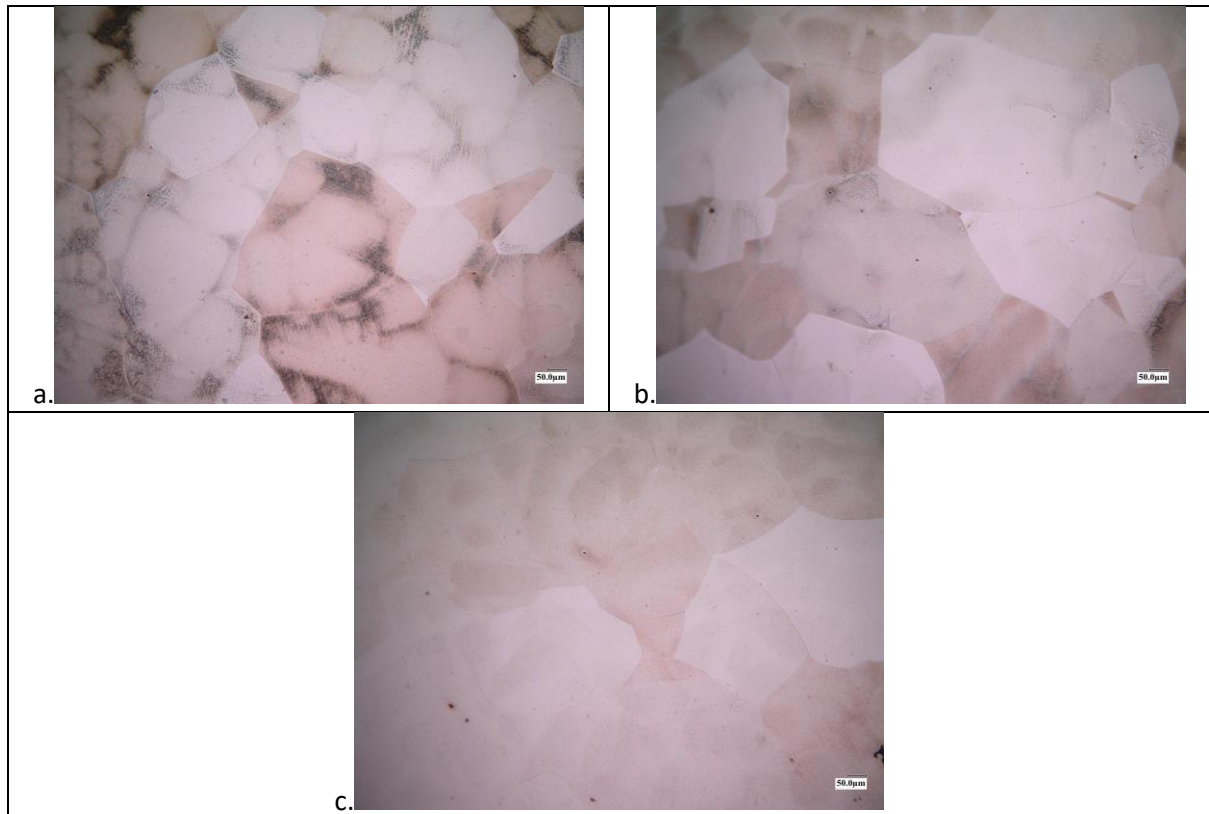


Figure 50 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after 600°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

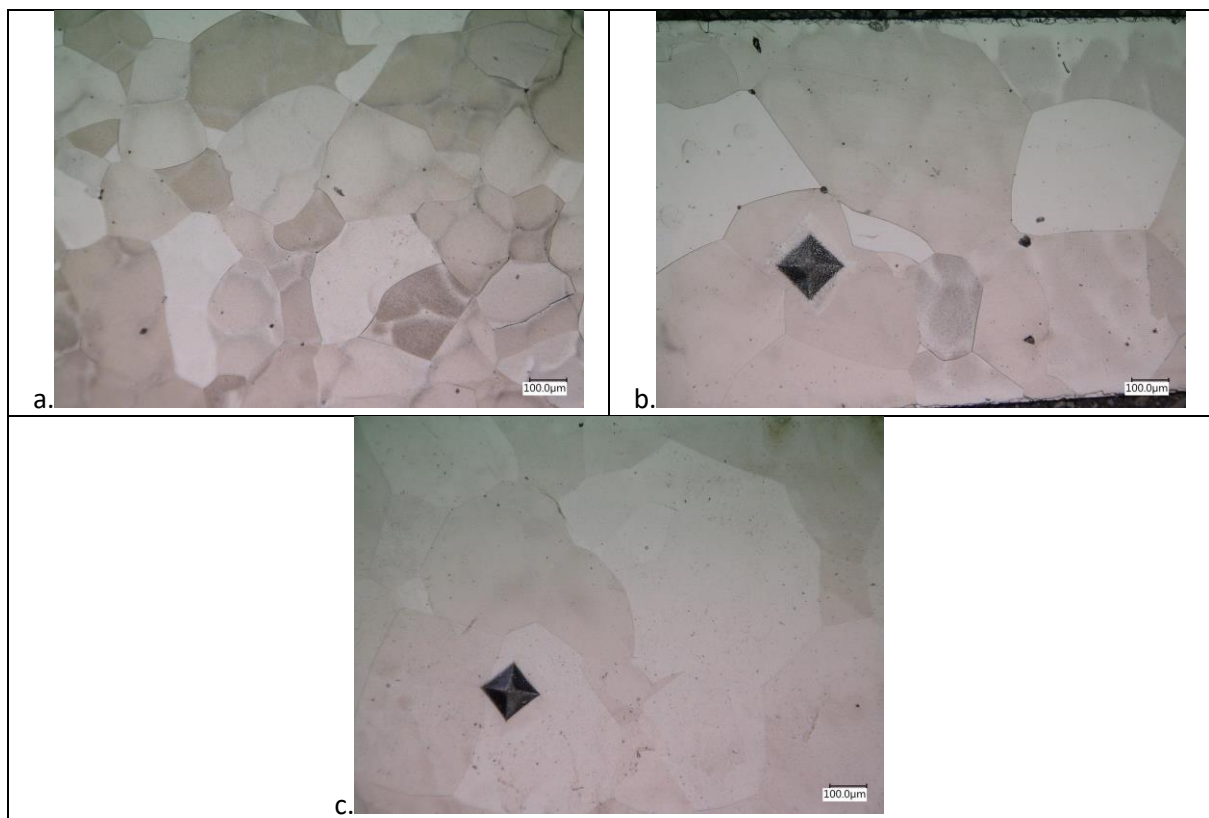


Figure 51 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after 800°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

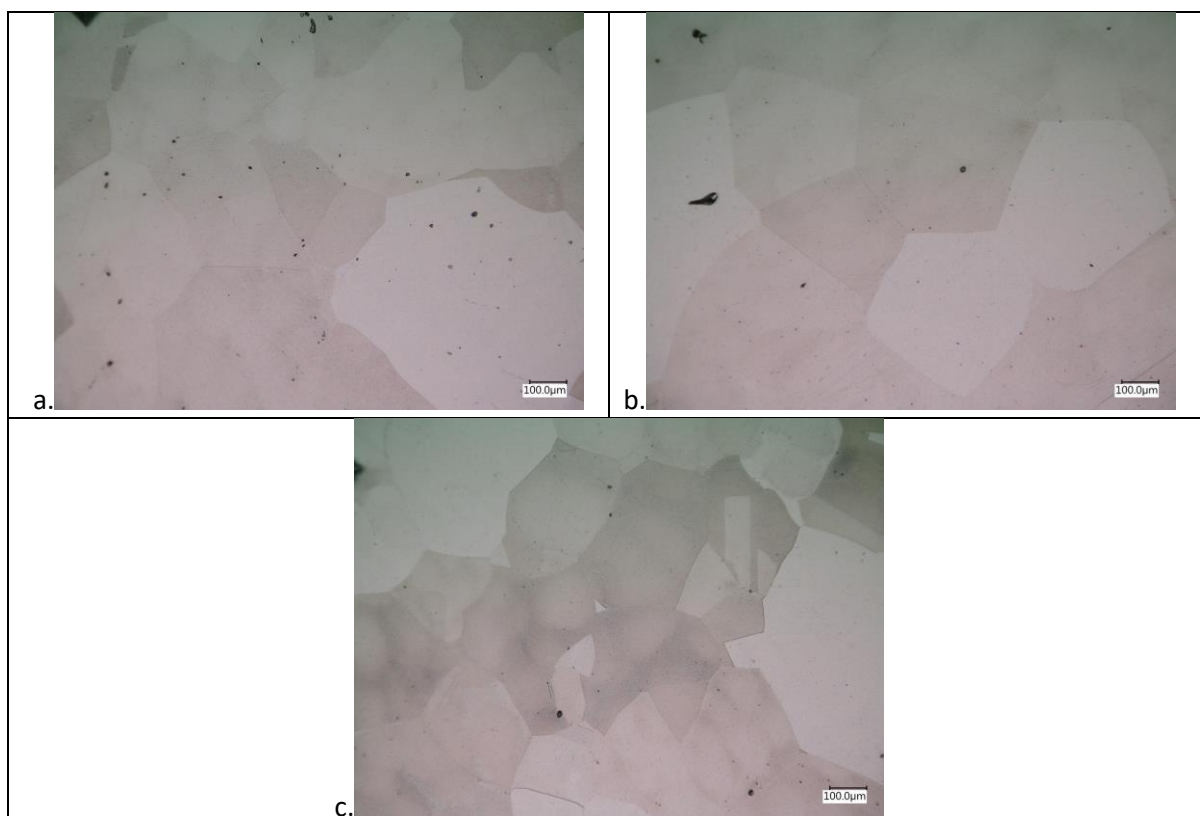


Figure 52 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after 950°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

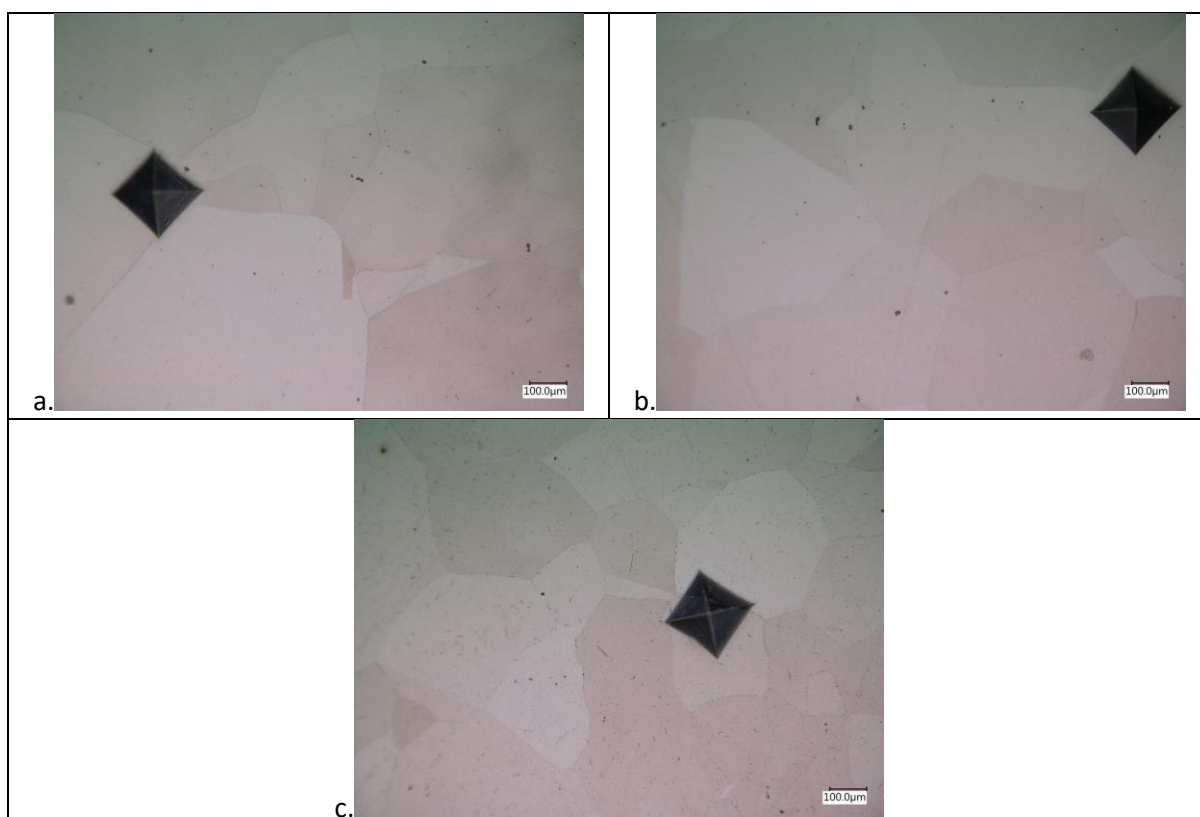


Figure 53 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after 1100°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

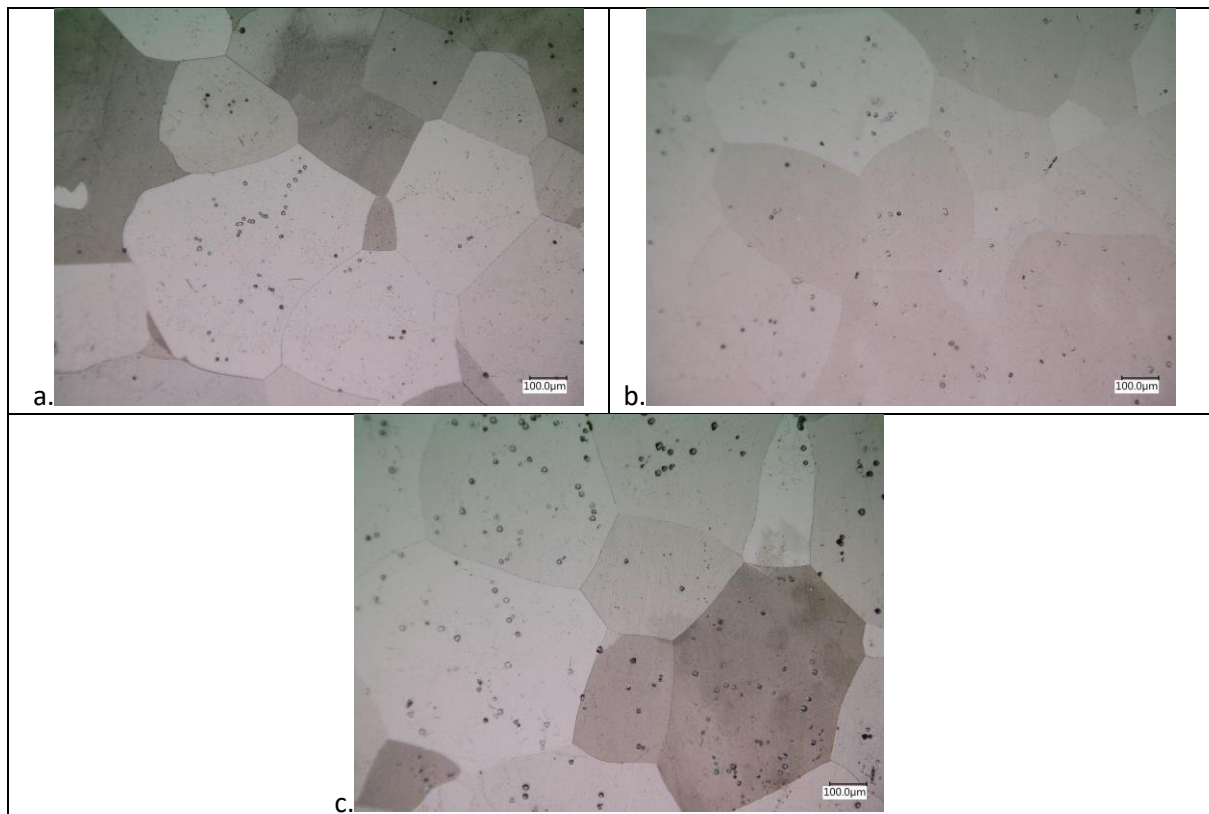


Figure 54 Optical micrographs of etched as cast FeNiCrCo high entropy alloy after 1250°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

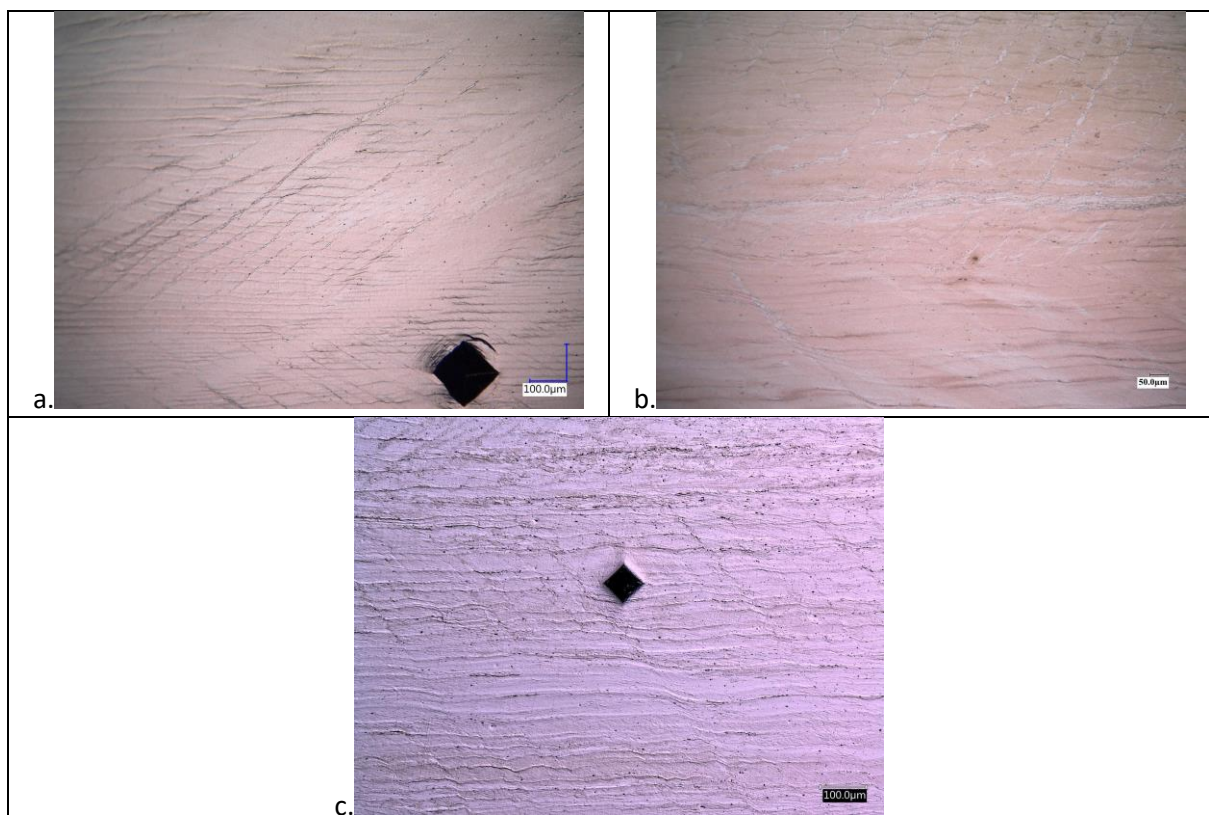


Figure 55 Optical micrographs of etched as rolled FeNiCrCo high entropy alloy after 600°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

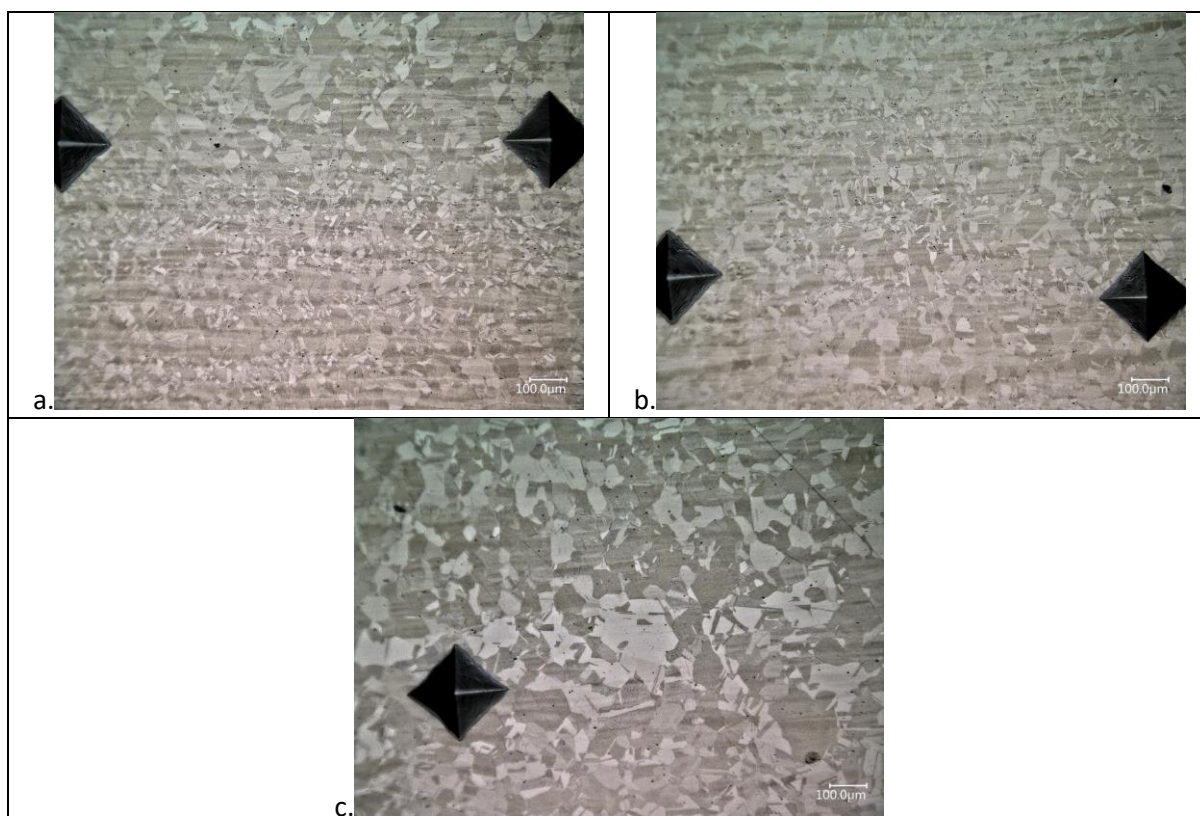


Figure 56 Optical micrographs of etched as rolled FeNiCrCo high entropy alloy after 800°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

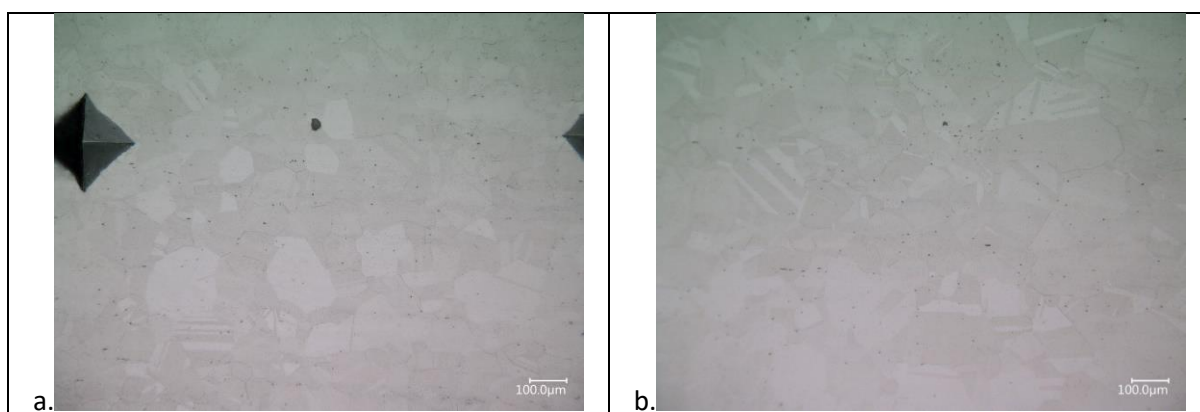


Figure 57 Optical micrographs of etched as rolled FeNiCrCo high entropy alloy after 950°C heat treatment for (a) 16 hrs (b) 72 hrs

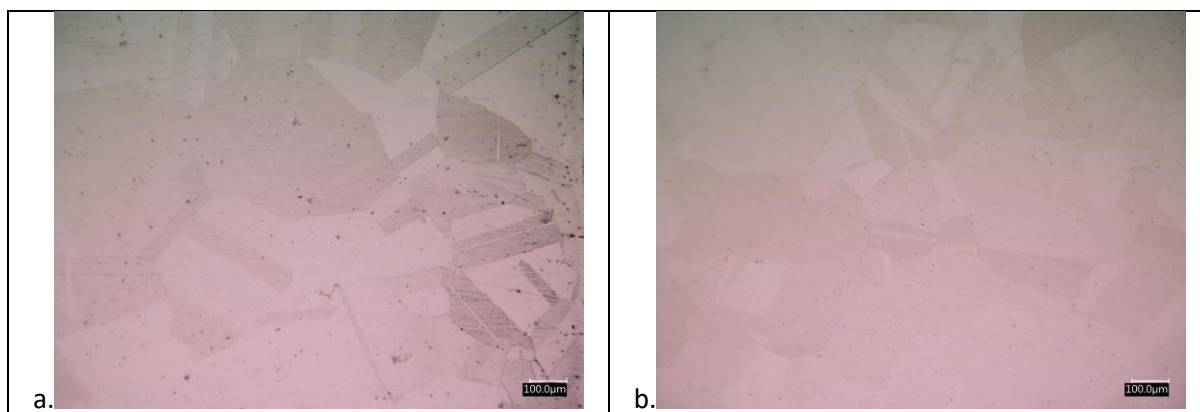




Figure 58 Optical micrographs of etched as rolled FeNiCrCo high entropy alloy after 1100°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

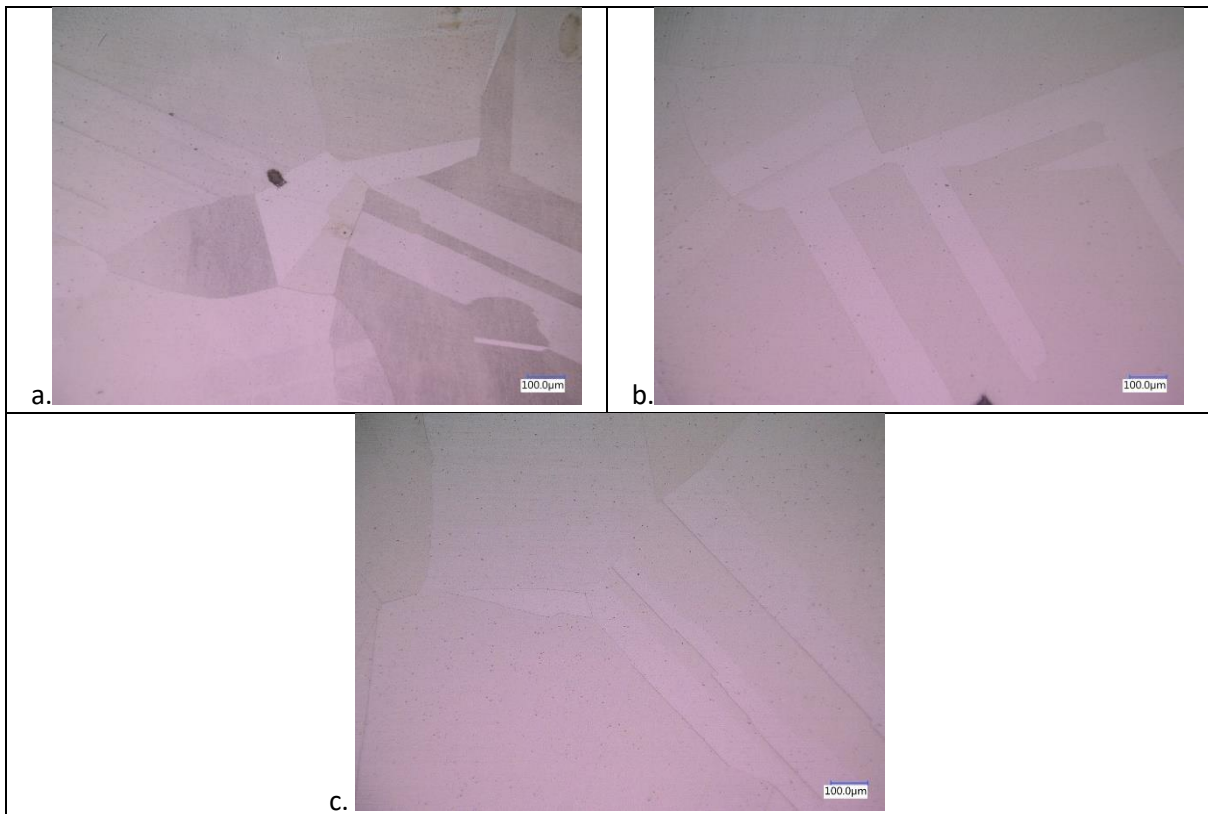
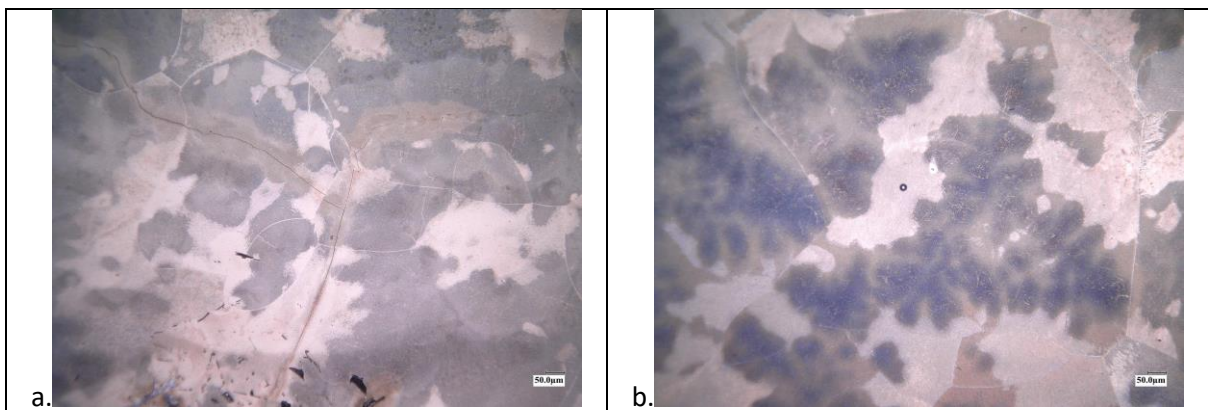


Figure 59 Optical micrographs of etched as rolled FeNiCrCo high entropy alloy after 1250°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs



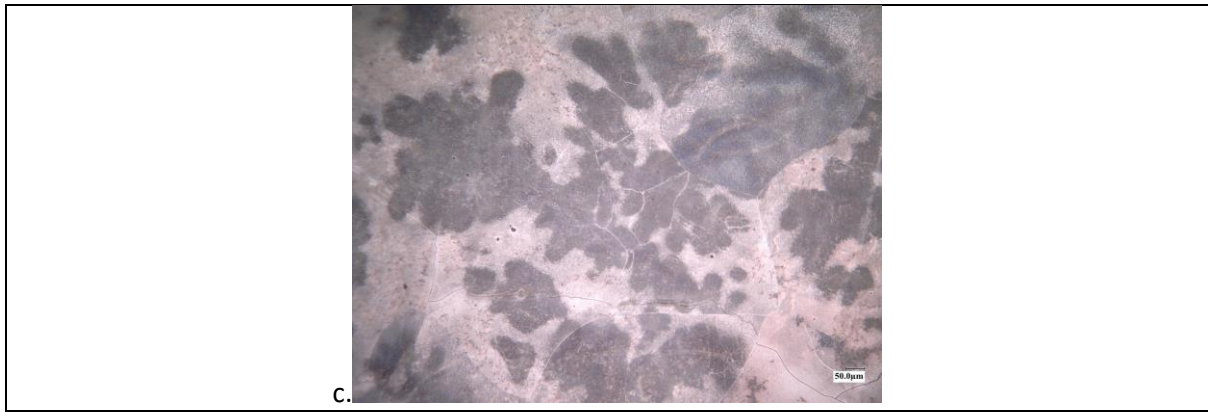


Figure 60 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy after 600°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

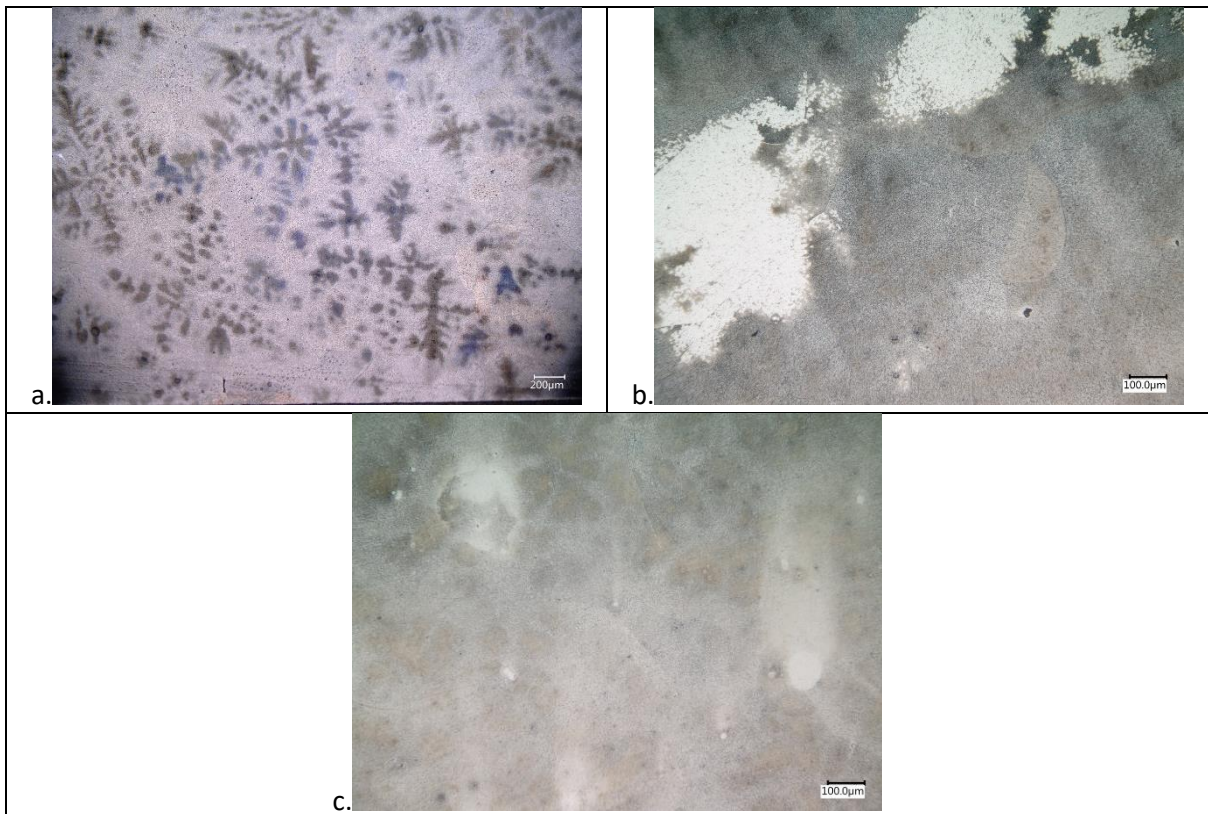


Figure 61 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy after 800°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

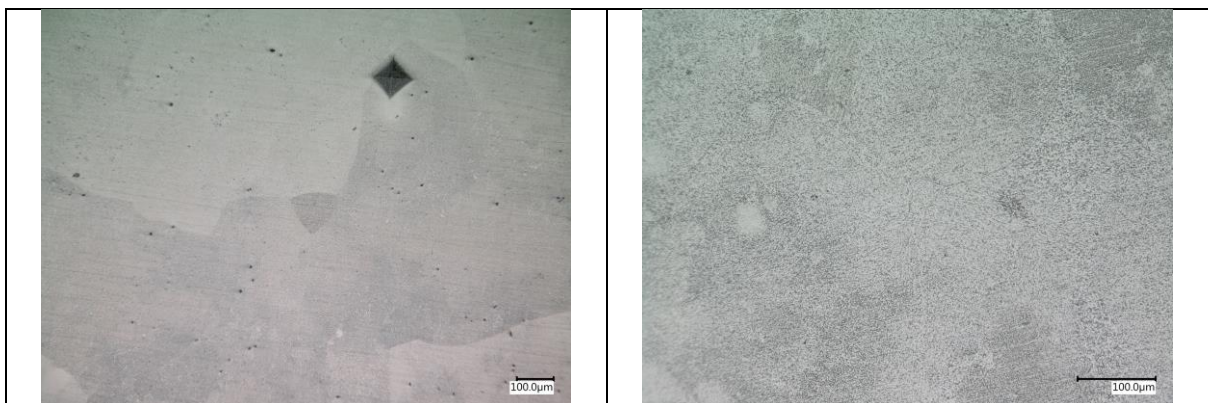




Figure 62 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy after 950°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

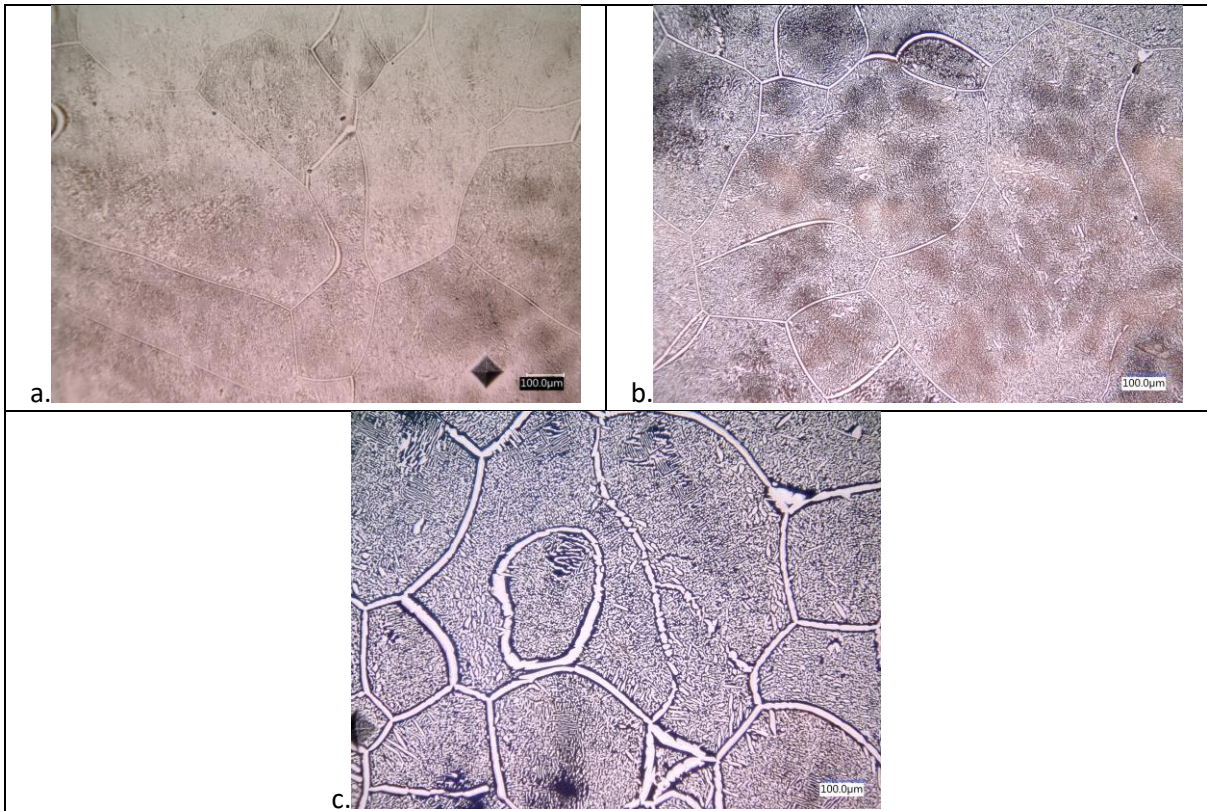
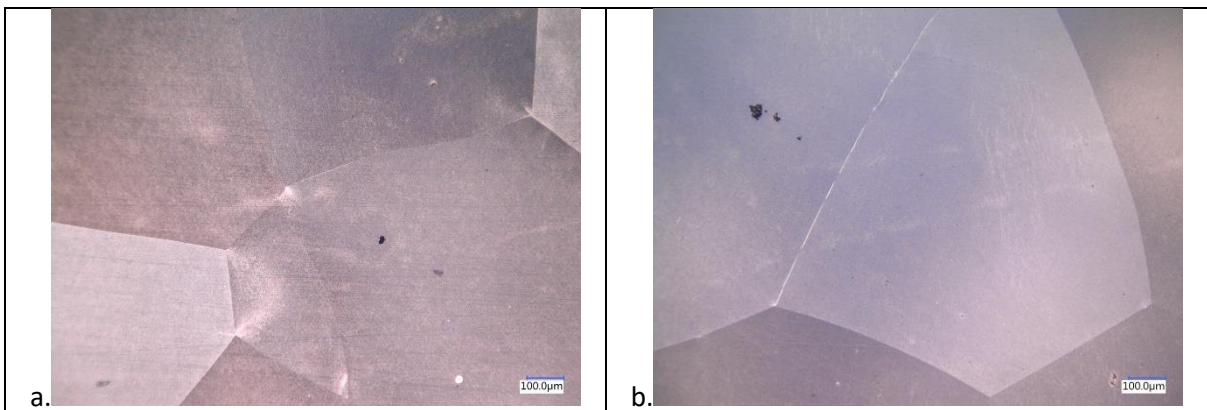


Figure 63 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy after 1100°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs



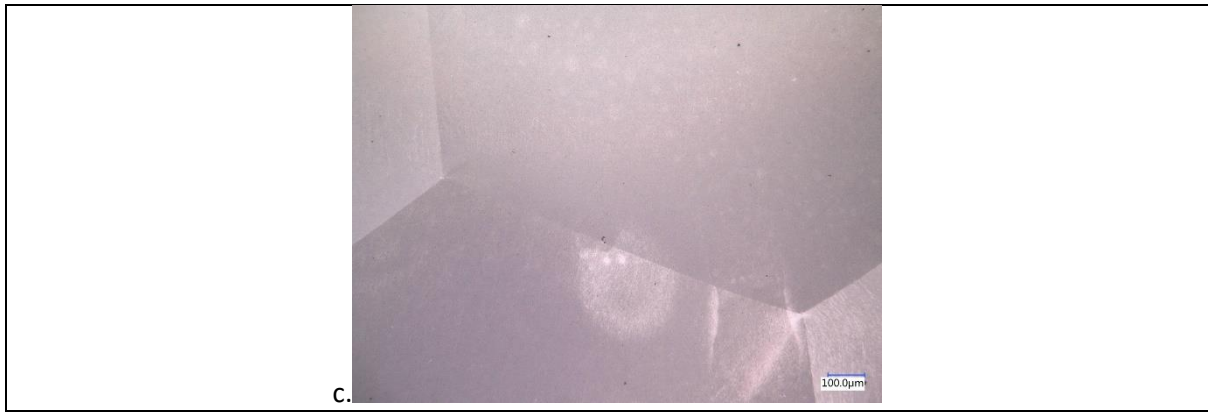


Figure 64 Optical micrographs of etched as cast FeNiCrCoAl high entropy alloy after 1250°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

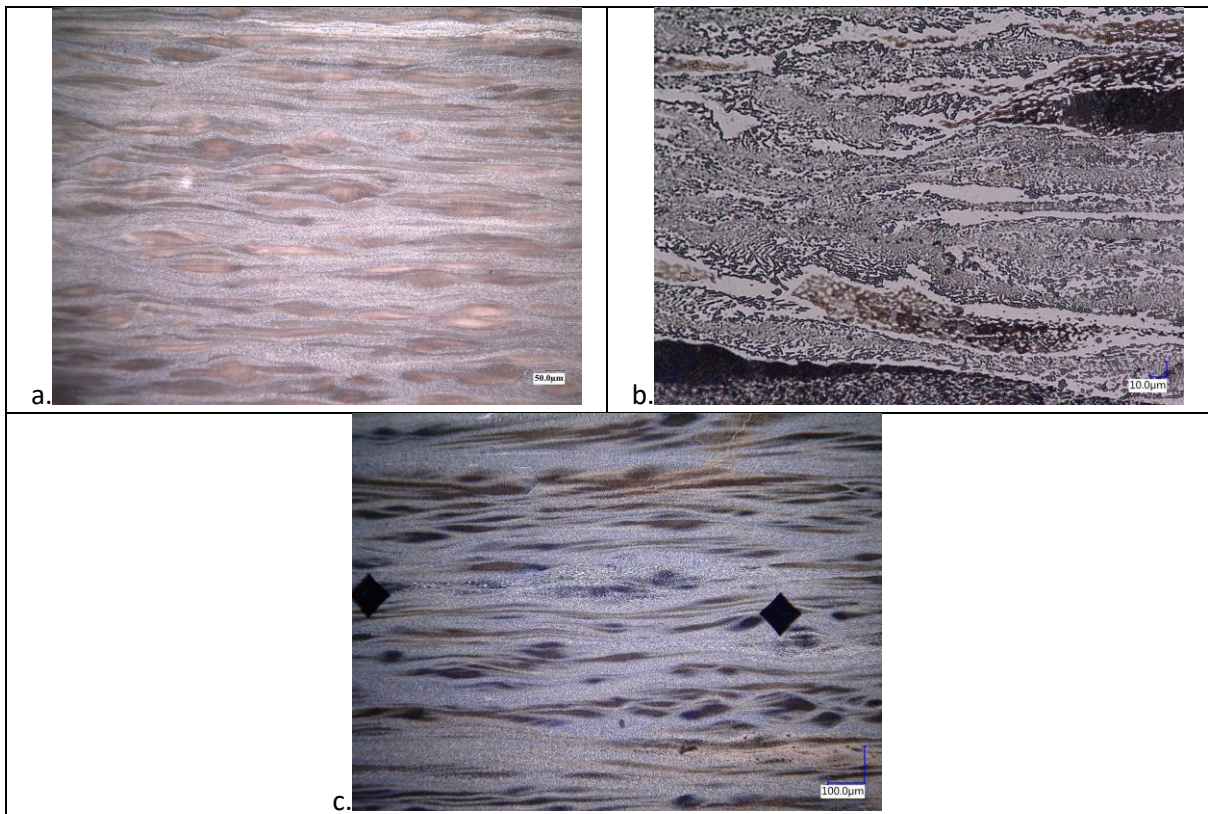


Figure 65 Optical micrographs of etched as rolled FeNiCrCoAl high entropy alloy after 600°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

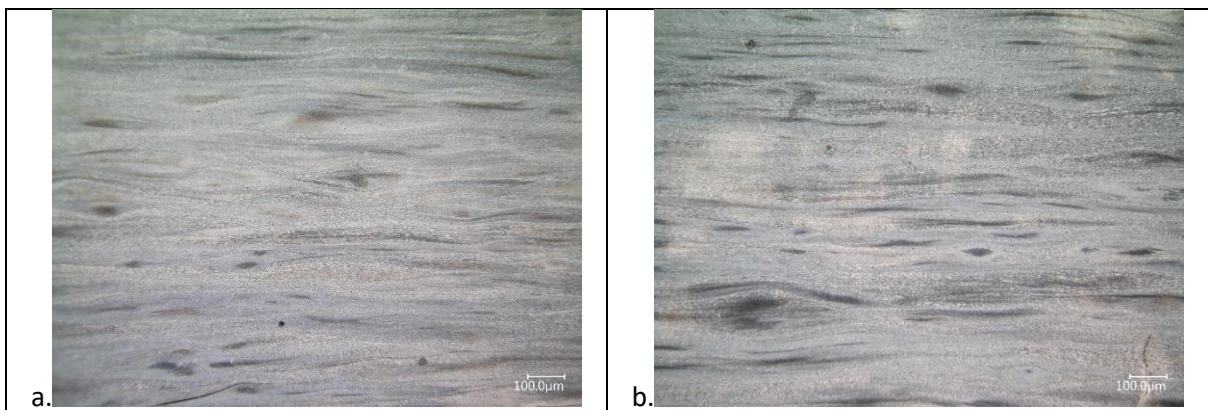




Figure 66 Optical micrographs of etched as rolled FeNiCrCoAl high entropy alloy after 800°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

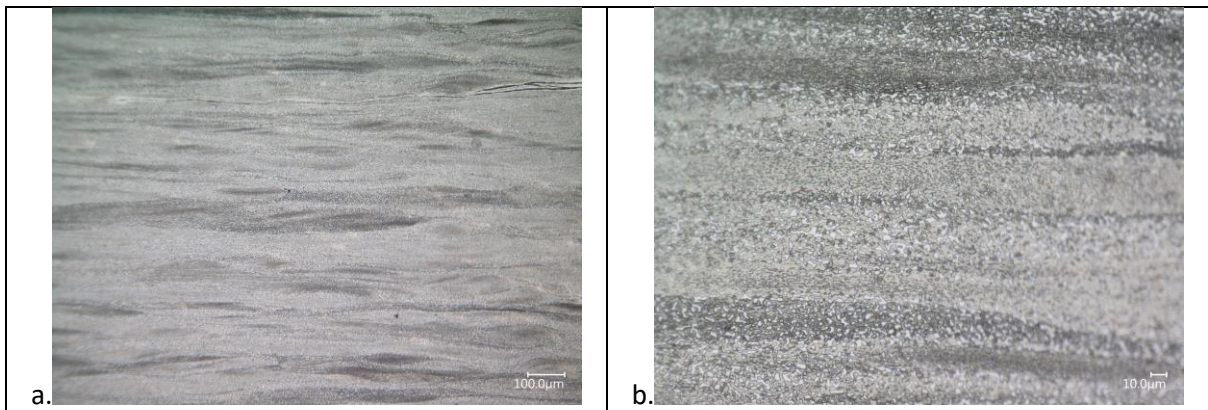


Figure 67 Optical micrographs of etched as rolled FeNiCrCoAl high entropy alloy after 950°C heat treatment for (a) 16 hrs (b) 72 hrs

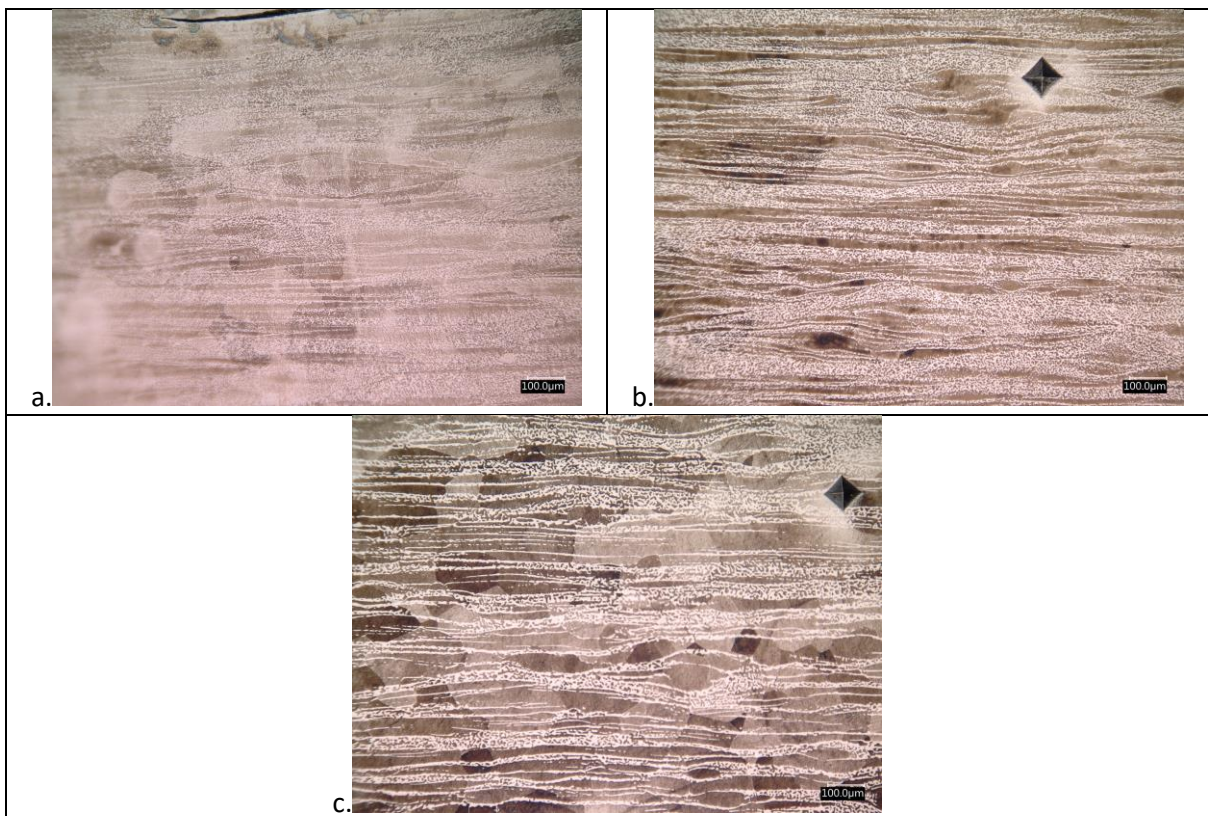


Figure 68 Optical micrographs of etched as rolled FeNiCrCoAl high entropy alloy after 1100°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

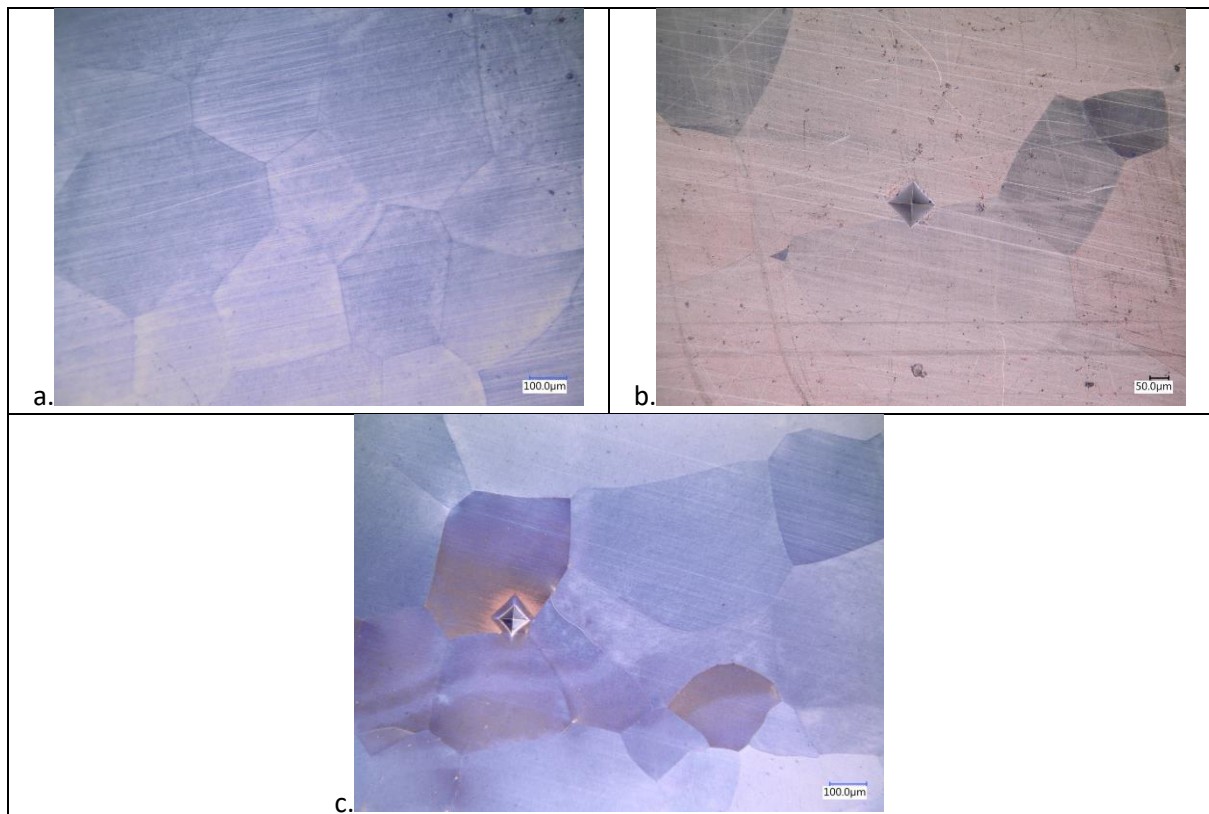


Figure 69 Optical micrographs of etched as rolled FeNiCrCoAl high entropy alloy after 1100°C heat treatment for (a) 16 hrs (b) 24 hrs (c) 48 hrs

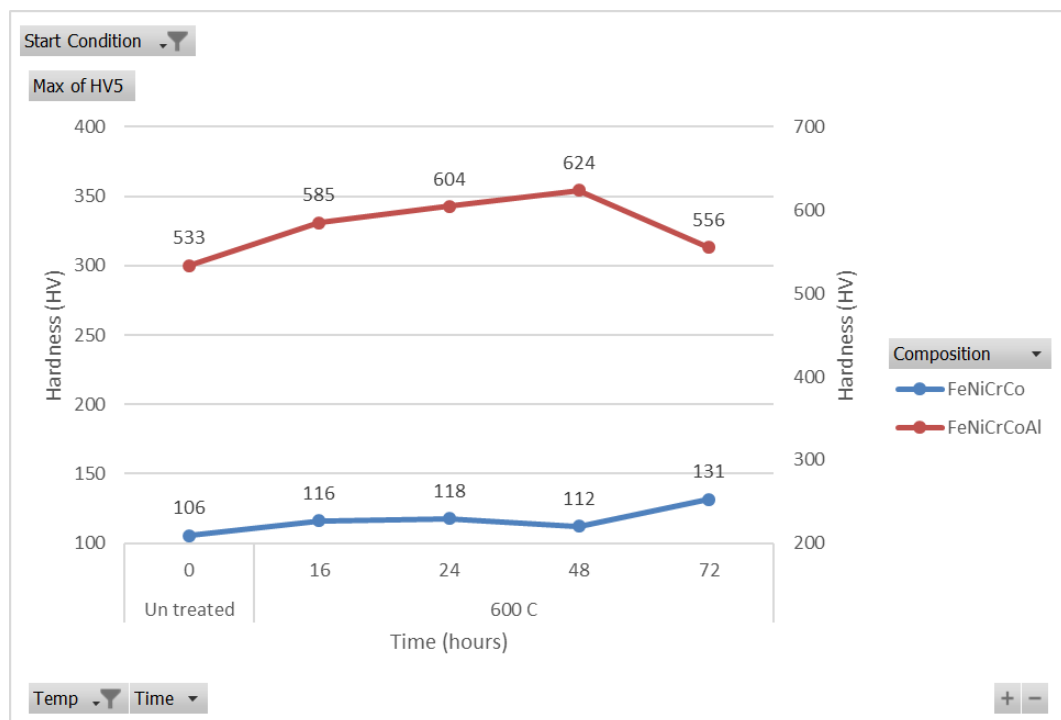


Figure 70 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl after 600°C heat treatment for different times

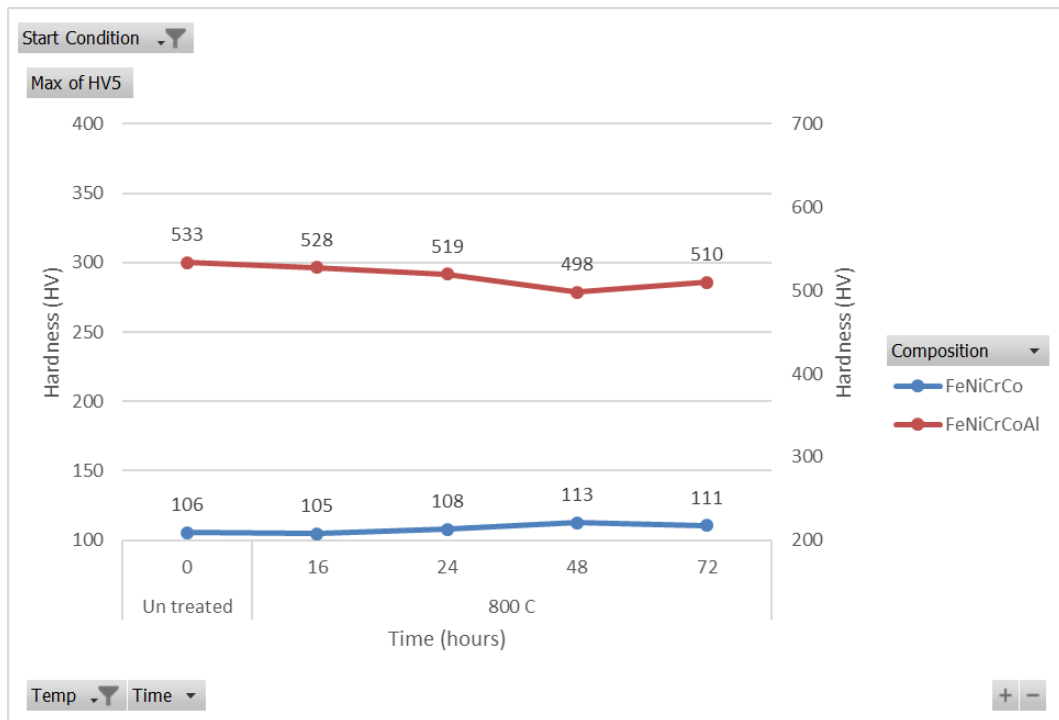


Figure 71 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl after 800°C heat treatment for different times

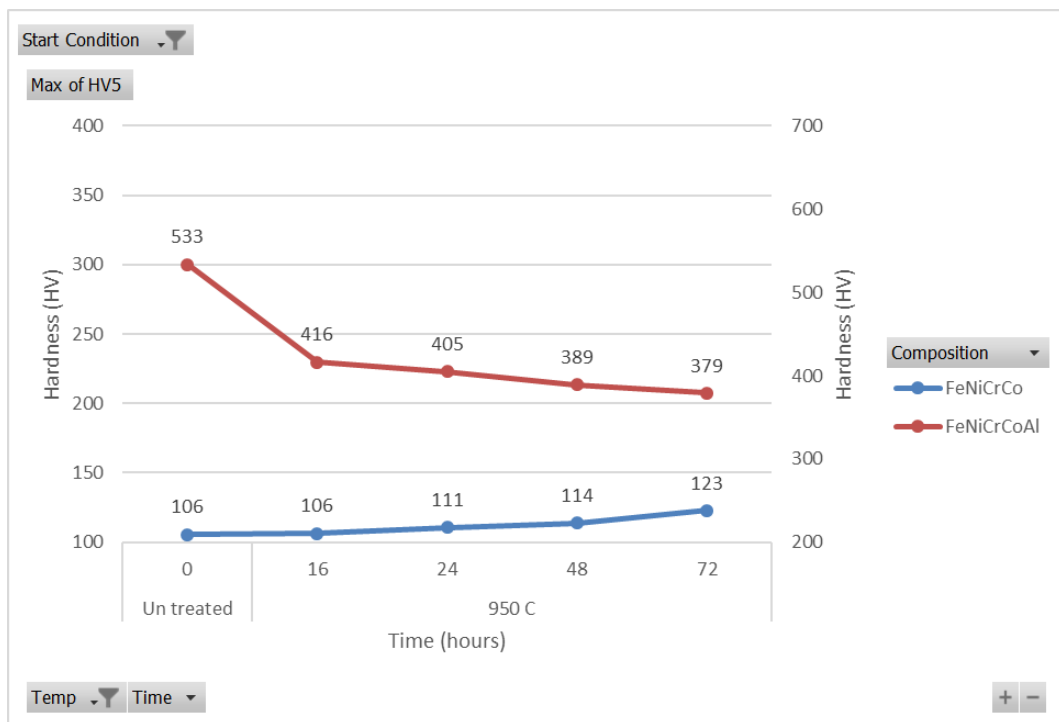


Figure 72 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl after 950°C heat treatment for different times

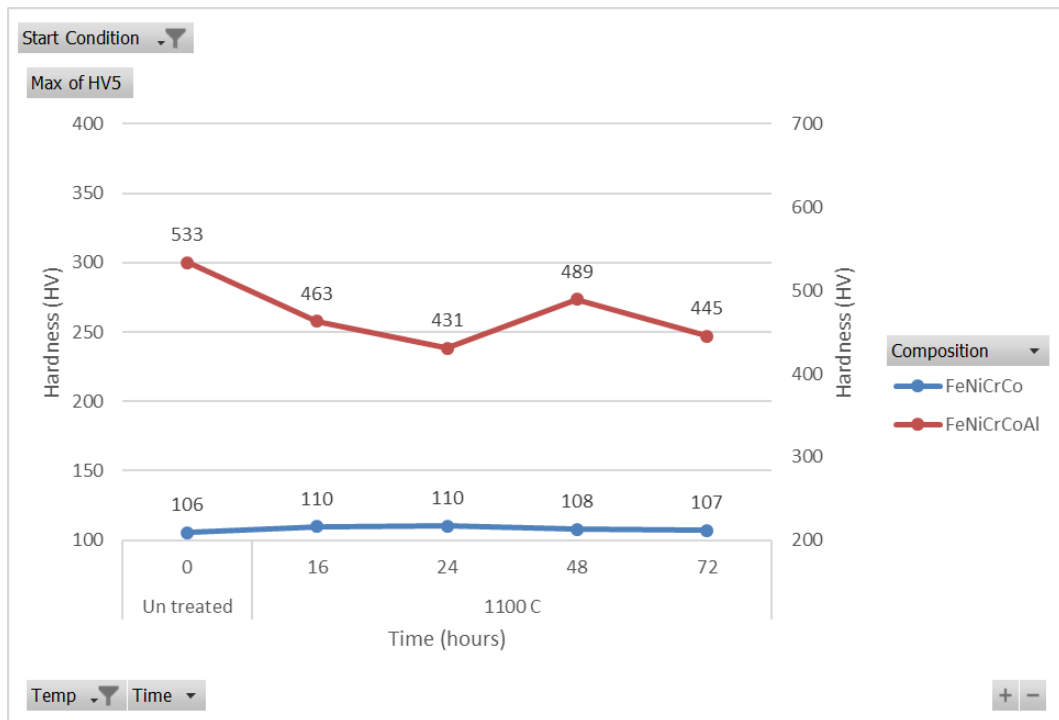


Figure 73 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl after 1100°C heat treatment for different times

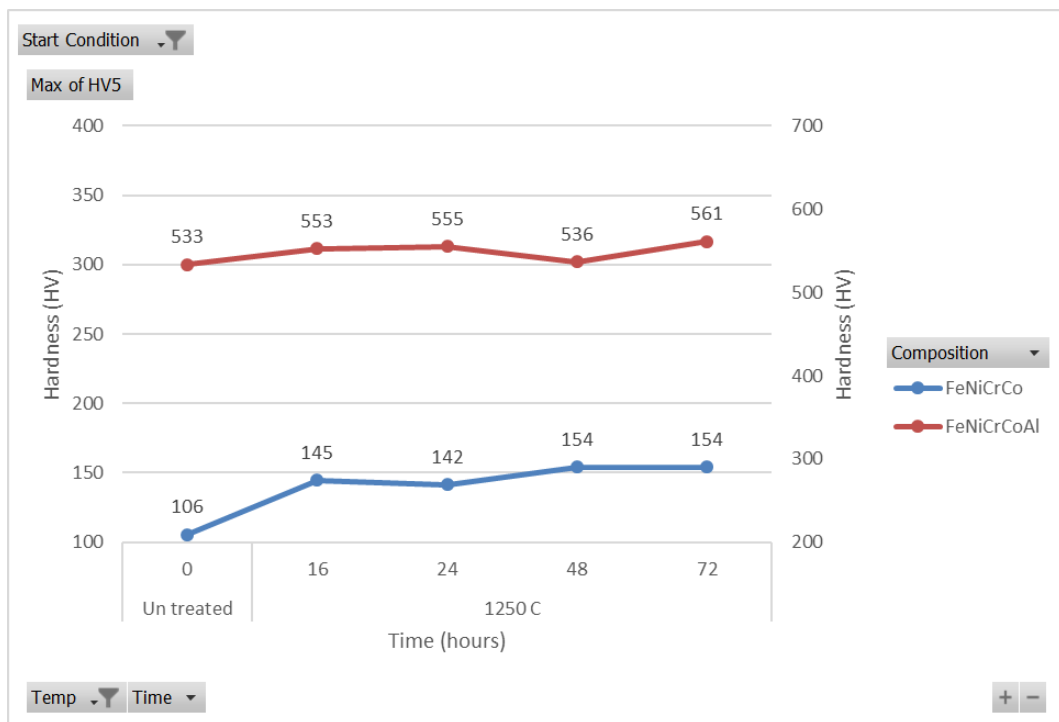


Figure 74 Hardness profile of as cast FeNiCrCo and FeNiCrCoAl after 1250°C heat treatment for different times

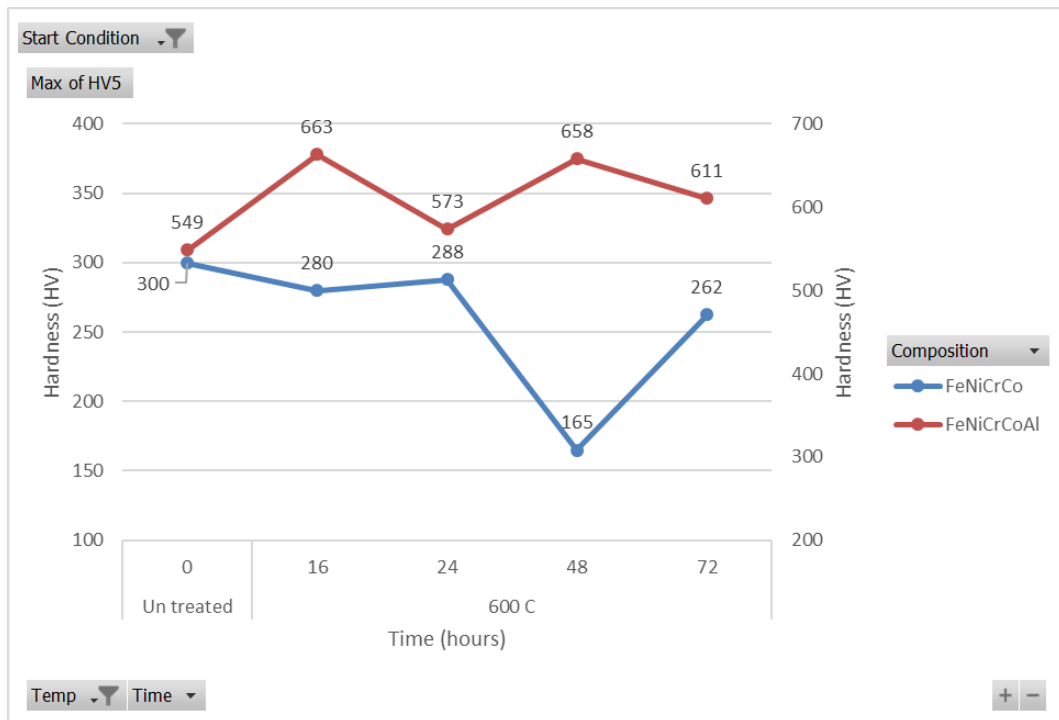


Figure 75 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl after 600°C heat treatment for different times

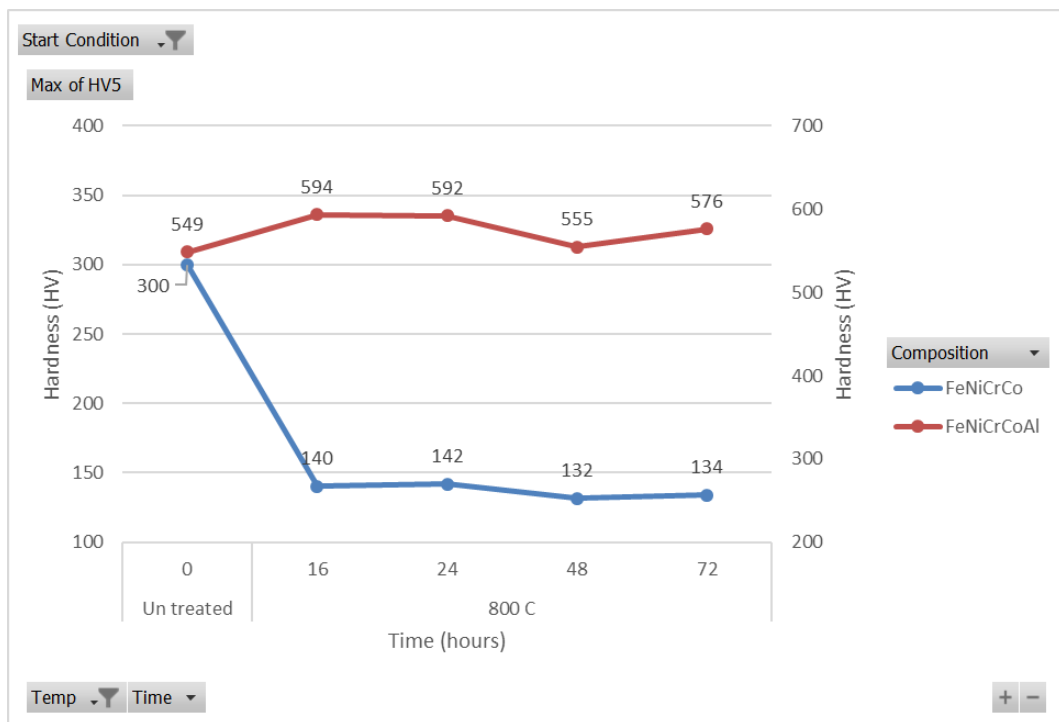


Figure 76 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl after 800°C heat treatment for different times

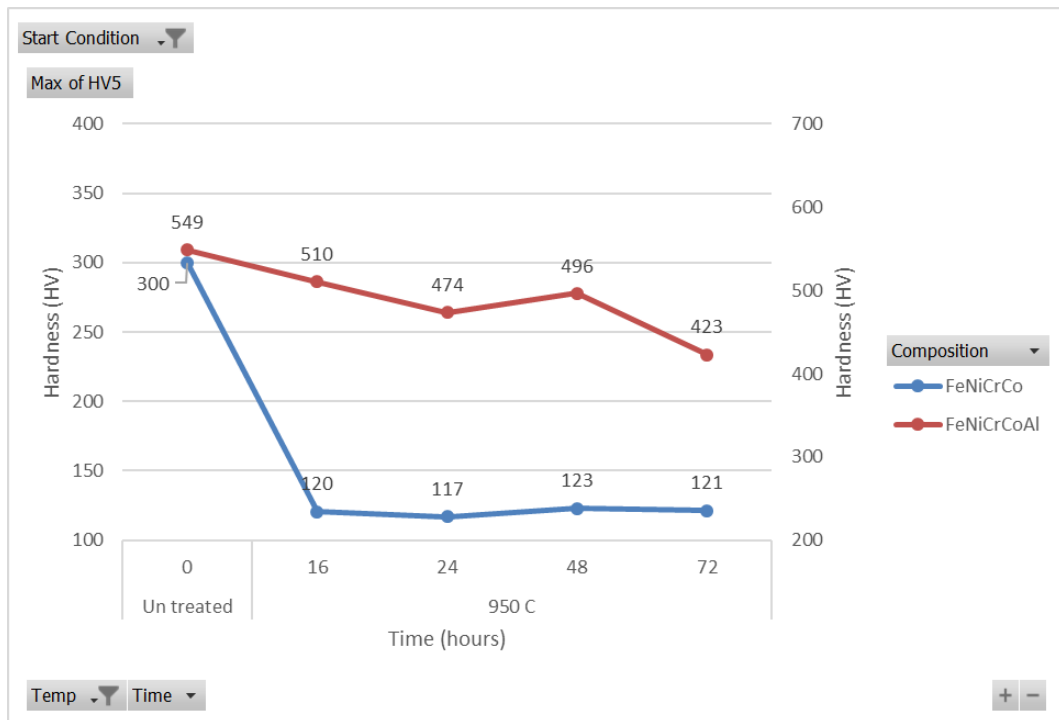


Figure 77 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl after 950°C heat treatment for different times

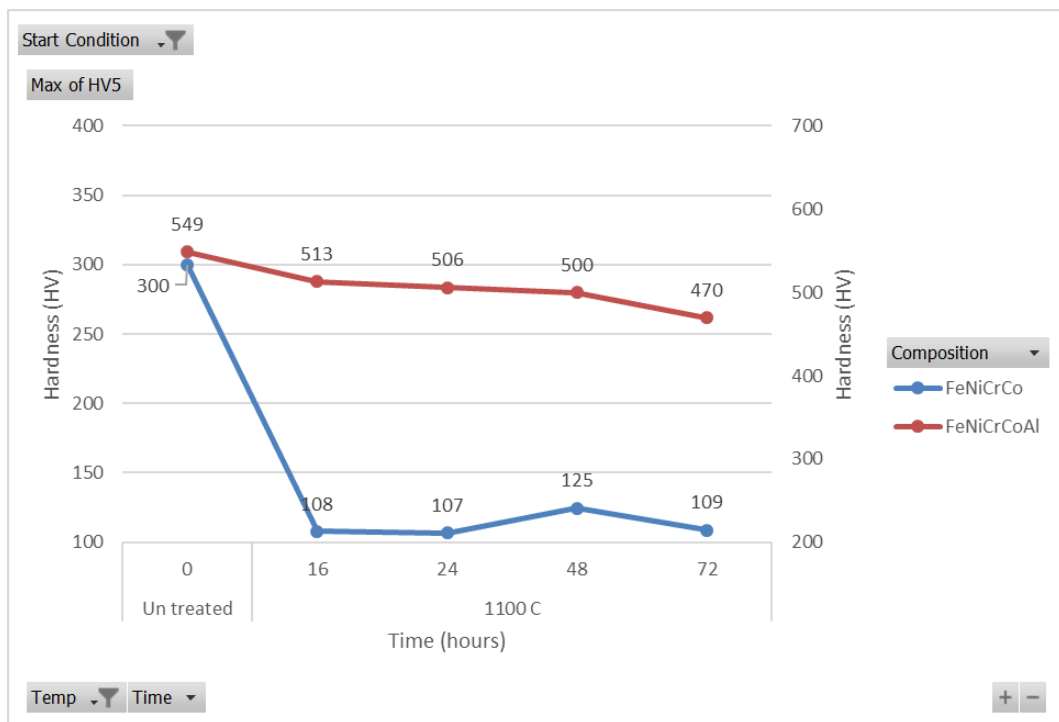


Figure 78 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl after 1100°C heat treatment for different times

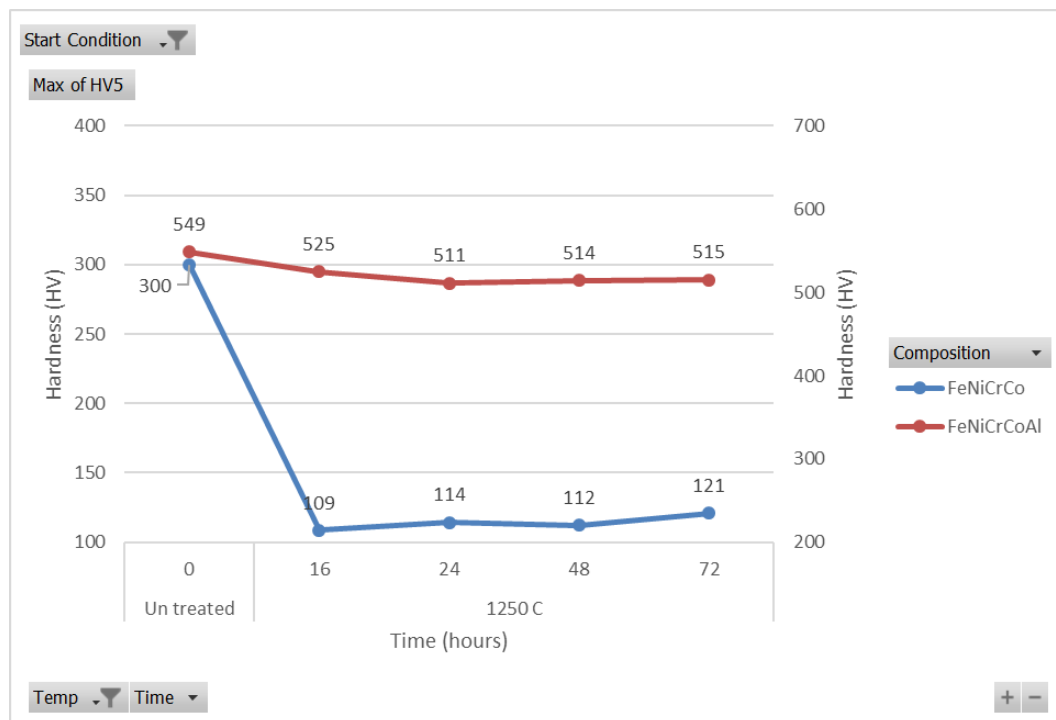


Figure 79 Hardness profile of as rolled FeNiCrCo and FeNiCrCoAl after 1250°C heat treatment for different times