Effect of processing routes on the Microstructure and Mechanical Properties of Novel High Entropy Alloys

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CERTIFICATE

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DEDICATION

We dedicate this thesis to our parents, our teachers, our siblings, our partners, and our friends who have been our constant guides and support throughout and helped us pave the way through thick and thin.

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ABSTRACT

High entropy alloys have garnered a lot of attention due to their impressive mechanical properties even at high temperature conditions compared to conventional alloys. In this study the High entropy alloys have been developed through two processing routes to understand the effect different processing conditions have on the resulting properties of the high entropy alloy. Electromagnetic levitation was used to process a NiCoCrNb high entropy alloy at low undercooling to form a high entropy alloy at equilibrium having FCC and Laves phase giving microhardness values of 800HV while Powder metallurgy route was used to make two NiCoCrNb samples at 18 hours of milling with 1050C sintering temperature and 28 hours of milling with 1100C sintering temperature. The 18hr-1050C sample showed improper sintering with high porosity and low densification; this resulted in low hardness values of 120HV. While the 28hr-1100C sample showed higher densification and higher hardness values of around 430HV which showed the formation of an HEA and proper sintering. The significant improvement in properties of the powder metallurgy samples in this study help us conclude that the powder metallurgy route offers promising results in improving the mechanical properties of the high entropy alloy with slight changes in processing parameter.

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KEY TO ABBREVIATIONS

BCC	Body Centered Cubic
BSE	Back-Scattered Electrons
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EML	Electromagnetic Levitation
FCC	Face Centered Cubic
HCP	Hexagonal Close Packed
HEA	High Entropy Alloy
MA	Mechanical Alloying
PM	Powder Metallurgy
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
VEC	Valence Electron Concentration
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

High entropy alloys (HEAs) were first developed by Yeh et al [1] and Cantor et al [2] [3] and have opened an array of variable properties which can be achieved in materials through slight compositional changes. Since they consist of 4 or more elements in relatively high concentrations (5-35 at.%) and equi-atomic quantities [4] the prospects have increased. The greater number of elements in high entropy alloys, as opposed to conventional binary alloys, increases the configurational entropy within the alloy system which decreases the Gibbs free energy of the system and thus stabilizes it. High entropy alloys have shown a large array of properties, their high strength and retentivity of mechanical properties at high temperature have made them attractive in the field of research.

High entropy alloys have gained popularity among researchers due to their ability to retain their high strength at high temperatures. The high strength of the alloy is explained by the lattice distortion which is caused by the atomic size difference between the elements in the alloy which results in hindering dislocation movement. High entropy alloys also are known to give superior properties than conventional alloys such as a higher strength to weight ratio, fracture resistance, yield strength, corrosion resistance [5].

Several HEAs have shown FCC or BCC single phase structures, though the presence of Nb in a high entropy alloy can form Laves phase which exists due to the size difference of atoms with Nb atoms [6]. FCC phase in HEAs has been observed to introduce ductility into the alloy along with low strength and BCC phase has been shown to introduce high strength and hardness but a lower ductility while Laves phase has good high-temperature strength and shows high potential for applications due to its promise in hydrogen storage materials. An ideal alloy would consist of a good ratio of these phases such that it provides good high-temperature strength as well as ductility.

Electromagnetic levitation (EML) and powder metallurgy are significantly different routes used for developing HEAs. Both of these routes help achieve different mechanical properties and varying microstructures. Electromagnetic levitation is a containerless solidification process that is used to melt the elements to form a homogeneous alloy, by providing low undercooling, at equilibrium without needing additional heat treatment. This route uses an inert environment for the whole process which means it contains the least amount of contaminations from its surroundings. Electromagnetic levitation also helps achieve low undercooling which forms an alloy at equilibrium state having eutectic lamellar microstructure. While powder metallurgy employs mechanical alloying, it forms an alloy through physical forces applied onto elemental powders at a solid-state without melting or heating the alloy. The impact forces used through ball milling can be the cause of contaminations from surroundings such as the milling balls or the container [7] [8] of the elemental powders, the milling medium used can also cause contaminations and thus any significant variations in the properties of the resulting alloy can be explained by the presence of these contaminations. The ability to change the processing parameters such as sintering time and temperature as well as the milling time give a greater control over the final properties of the alloy which can be achieved. The powder metallurgy route helps develop the alloy at lower processing temperatures and thus is more energy efficient. The electromagnetic levitation process is a lab scale route used to understand the properties of high entropy alloy samples but can’t be used to process a bulk sample on the other hand Powder metallurgy can be used to form any size sample and the process is thus easy for commercialization. Powder metallurgy processing route can also be modified to cater to any shaped product which the EML method fails to cater as the samples will always be spherical due to the levitation of the small sample.

In this paper, we observe the changes in microstructure and mechanical properties of the NiCoCrNb alloy system with changes in process parameters such as sintering temperature and ball milling time with comparison to the solidification route of processing.

The resulting alloys are then compared for their microstructure and mechanical properties. The testing and characterization techniques used are scanning electron microscopy (SEM), X-ray diffraction (XRD), Energy Dispersive X-Ray Analysis (EDX), and microhardness testing which will provide information about the phases and intermetallic compositions formed in the microstructure and the hardness of the alloy.

CHAPTER 2

LITERATURE REVIEW

2.1 High Entropy Alloys

2.1.1 Thermodynamics and phase formation criteria

High Entropy Alloys are alloy systems consisting of four or more than four elements in near equimolar concentrations. Mixing of a larger number of elements increases configurational entropy and stabilizes the system by lowering the Gibbs free energy, as dictated by the equation,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Using equal atomic percentage of all elements makes the system reach maximum configurational entropy, and turns the following entropy equation,

$$\Delta S_{mix} = -R \sum_{i=1}^{N} ci \ln ci$$

where c_i is the molar concentration of the i^{th} component, into

$$\Delta S_{mix} = R \ln N$$

relating entropy of mixing simply to the number of elements constituting the system.

The enthalpy of mixing, along with atomic size difference (δ) and valence electron concentration (VEC) are also important factors. The equations to calculate these values are as follows:

$$\Delta Hmix = \sum_{i=1, i\neq j}^{N} 4\Delta H_{AB}^{mix} c_i c_j$$

$$\delta = \sqrt{\sum_{i=1}^{N} c_i \left(1 - r_i \middle/ \sum_{i=1}^{N} c_i r_i\right)^2}$$

$$VEC = \sum C_i VEC_i$$

For the formation of a simple solid solution in the HEA, -15kJ/mol < ΔH_{mix} <5kJ/mol and $\delta < 4\%$ are the criteria. Here it is also important to note that ΔH_{mix} values below -15kJ/mol are of significance as they indicate the formation of intermetallic phases such as the hard Laves phase. This will be discussed in greater detail later. Valence electron configuration defines which phase/ phases are likely to form. VEC values smaller than 6.8 indicate the formation of a BCC phase, values greater than 8 indicate the formation of FCC phase, while values in between the two show that either or both phases can form. [9]

2.1.2 Factors affecting HEAs

Due to their multi-component nature, four core effects exist in high entropy alloys.

1. **High entropy effect**

As explained in section 2.1.1, thermodynamics, the high entropy produced in the system, stabilizes the phase by decreasing the Gibbs free energy. Due to this effect, HEAs defy the Gibbs phase rule,

$$P = C + 1 - F,$$

and usually exist as single phase or two-phase structures. Under this same effect, the stability of HEAs increase at higher temperatures, unlike most conventional materials. The higher entropy at high temperatures stretches the solubility range and resists phase separation and intermetallics formation [10].

2. **Sluggish diffusion effect**

During the formation of the alloy, the atomic size difference and the difference in energy gaps existing between different areas hinder the diffusion of atoms. This slow diffusion effect is commonly used to explain the formation of nanoprecipitates in HEAs. Nanoprecipitates, in turn lead to many favourable mechanical properties in the structure, for example high creep resistance, high toughness and high recrystallization temperatures.

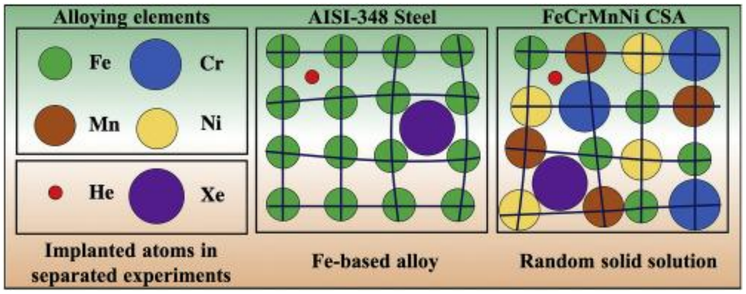

Figure 1 Comparison of potential of diffusion between lattices of a conventional alloy and a high entropy alloy

**For interpretation of the references to colour in this and all other figures, the reader is referred to the electronic version of this thesis*

The image shows the great variation in the lattice dimensions of a random solid solution, in comparison to a conventional steel alloy, and how it makes it nearly impossible for diffusion to occur. It can be seen that it is difficult for both large and small impurities to diffuse through such a structure.

3. Severe lattice distortion effect

As higher entropy alloys do not have a principal element, as is the case with conventional alloys, all elements are equally likely to occupy a lattice position. Since all elements have different sizes the above leads to severe lattice distortion. This effect is also the reason behind scattering and thus, smaller XRD intensities in HEAs. Lattice distortion hinders the movement of dislocations which results in high hardness and strength in the structure. Likewise, it can also be related to the property of tensile brittleness in HEAs. But overall, this effect also contributes to the decrease of temperature dependence of the above-mentioned properties [11]

4. Cocktail effect

The cocktail effect means that due to having multiple principal elements, the properties obtained in HEAs can be unexpected or exaggerated compared to conventional alloys. It is also easier to control these properties as a slight change in composition produces a magnified effect in properties. The cocktail effect can be used to control alloy properties such as hardness, modulus and even crystal structure. An example of this is the change in crystal structure from FCC to FCC+BCC to BCC in HEAs with increasing Aluminium content [12].

2.1.3 Effect of Temperature on High Entropy Alloys:

Upon application of high temperature on high entropy alloys volume expansion can be observed but the high entropy alloy remains stable [Structural stability of high entropy alloys under pressure and temperature]. The stability of High entropy alloys can only be explained through their high entropy. As increasing temperature also increases the disorder within the system which thus increases entropy (which can be understood clearly through the thermodynamic phase formation criterias discussed in 2.1.1) the stability of the alloy must increase as the Gibbs free energy decreases further. Thus we deduce that increase in temperature increases the stability of high entropy alloys.

2.1.3 FCC and BCC phases in HEAs:

There are many factors which determine the hardness values of the high entropy alloys and the respective FCC and BCC phases in the microstructure.

2.1.3.1 FCC Structure Properties:

FCC structure is known to be very ductile due to its many slip planes. The slip exist in closed packed planes in the crystal structure. This reduces the critical stress for FCC planes which makes it more ductile. The slip plane in FCC is {111} and its slip direction is <110>. In total FCC structure has 12 slip systems, the magnitude and direction of the slip are represented by Burgers Vector.

In HEA the FCC structure usually consist of Ni metal which gives the alloy high ductility and this property exist even at very low temperature. If a hetero structure consists of ductile FCC phase and any other hard structure then it would result in high strength of the alloy.

2.1.3.2 BCC Structure Properties:

BCC phase is known to be harder than FCC because it does not have proper closed planes. BCC phases have more slip planes than FCC but due to lesser closed planes its slip is not easy. There are up to 48 slip systems in BCC but it requires energy to move due to which it gives strength to this phase. The hardness of BCC arises due to this reason which makes BCC harder phase. The BCC phase is stronger than the FCC phase in several alloy systems, such as AlxCoCrCuFeNi, Al0.5CoCrCuFeNiVx, and AlxCoCrFeNi, which can be explained with the basic structure factor and solution-hardening mechanism. The hardness of the hetero structure containing FCC and BCC phase can be calculated by the following formula.

$H = aH_{FCC} + (1 - a)H_{BCC}$

Where H_{FCC} and H_{BCC} are the average hardness of these phases, a is the volume fraction of FCC structure and (1-a) is the volume fraction of BCC phase. An example of this is shown in figure 2 where hardness increases as bcc character in the alloy increases with aluminum addition.

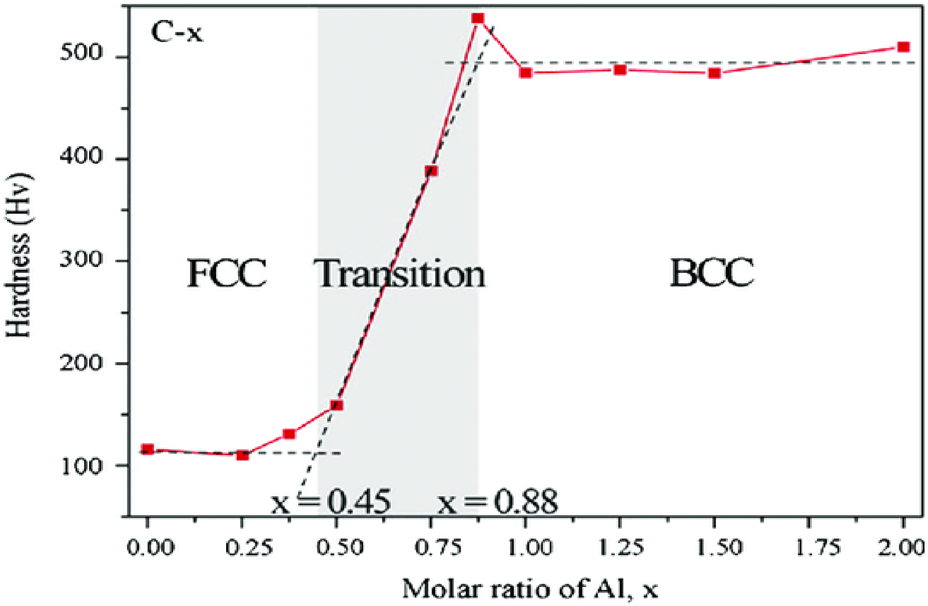

Figure 2 Graph of hardness against molar ratio of Al for CoNiCrAlxFe alloy

2.1.4 Eutectic High Entropy alloys:

Research has shown that eutectic high entropy alloys possess the benefits of both high entropy alloys as well as eutectic alloys are easily castible and form uniform, fine microstructures [13]without requiring any post solidification heat treatments giving good strength to ductility ratio even at high temperatures.

We get such advantages from the eutectic high entropy alloy because it possesses features such as, near-equilibrium microstructure that gives properties which remain unchanged with increase in temperature even at temperatures as high as their reaction temperatures, they give low energy phase boundaries, great control over microstructures of the alloy along with high rupture strength and stable defect features. The formation of eutectic high entropy alloy helps achieve good high temperature creep resistance and the regular lamellar rod-like eutectic microstructure forms a sort of in-situ composite. [14]

The solidification method helps us study the formation of the microstructure through which we can understand the formation of the pro-eutectic composition in the form of dendrites and the composition surrounding the dendrites which solidifies at eutectic composition forming a lamellar microstructure. The undercooling of the melt causes the formation of dendrites in the melt such that the dendrites solidify at the proeutectic composition leaving a melt having eutectic composition in the interdendritic region which then solidifies forming a lamellar microstructure.

2.1.5 Formation of Laves phase in HEAs

Laves phases are intermetallic phases in the form $AB_{2.}$ Here the lattice positions are occupied by A atoms while, the tetrahedral interstitial sites are taken up by the B atoms. According to the phase formation criteria in HEAs, the laves phase forms when the value of thermodynamic parameters $\Delta H_{mix} < -15$kJ/mol and $\delta > 5\%$. Enthalpy of mixing is usually this low when refractory metal atoms are mixed with other metal atoms. Therefore, addition of metals such as Tungsten, Molybdenum, Niobium and

Titanium leads to the formation of this phase. Occurrence of the Laves phase induces properties such as high hardness and wear resistance in the structure. It is especially beneficial in FCC structured HEAs where it balances the soft FCC phases.

2.2 Electro-magnetic levitation

2.2.1 EML Principle

In the process of alloying using Electromagnetic levitation, an alternating magnetic field is developed by the flow of high frequency AC current through both coils. This gives rise to eddy currents in the sample. The first effect of this is that the sample thus gets heated up due to its internal resistance. Secondly, because of the eddy currents, the sample develops its own magnetic field, opposite in direction to the primary magnetic field from the coils. The interaction between the eddy currents and this magnetic field produces Lorentz forces. Due to opposite magnetic fields, the sample experiences repulsion from all sides and hence gets levitated.

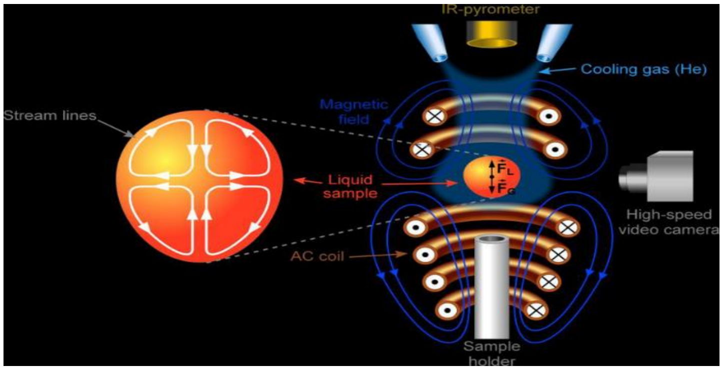

Figure 3 Electromagnetic levitation of melt showing magnetic field lines that induce eddy currents

During levitation, the sample goes through continuous vibration & rotation due to the alternating current changing direction, which changes the direction of the force. This movement results in thorough mixing of the alloying elements in the liquid melt.

Electro-magnetic levitation is an example of contact-free processing for alloy development.

2.2.2 Solidification

Along with the exceptional mixing, another advantage of EML is that it is an ultra-pure process. The solidification takes place in the levitated state. Due to the non-contact nature of the process, heterogenous nucleation at the container walls is prevented and contamination of the alloy is avoided. Using a fast solidification rate does not allow time for diffusion to occur and would result in a non-equilibrium structure. In order to achieve a stable, equilibrium structure slower solidification rates can be employed.

2.2.3 Undercooling and Homogenous Nucleation

Heterogenous nucleation starts with the deposition of atoms on a foreign surface, after which growth occur and solidification commences. On the other hand, homogenous nucleation is the formation of nuclei without any foreign surfaces or particles. Due to the absence of foreign surfaces in this case, energy barrier is too high for nucleation to start. For this reason, the melt is momentarily cooled below the freezing point where nuclei form.

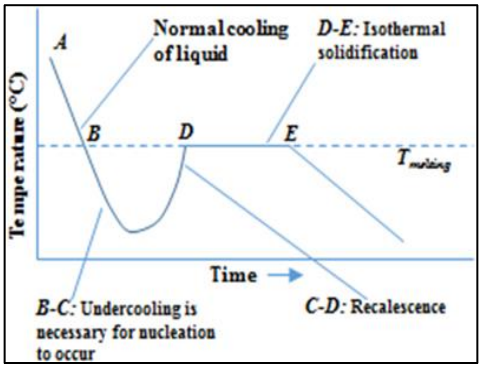

Figure 4 Graph showing undercooling and recalescence during a cooling cycle

This process is known as undercooling of the melt. Once nuclei have formed, the temperature can again be increased to above the freezing point and the normal cooling process can be resumed so that growth occurs on the nuclei and the melt solidifies.

A high undercooling (larger temperature drop) speeds up solidification without allowing time for diffusion. Instead, a low undercooling induces homogenous nucleation only and any significant grain growth occurs only after the recalescence. This leaves time for appreciable diffusion to occur.

2.2.4 Eutectic Solidification

A eutectic phase is one which forms after phase transformation at a single temperature rather than a solidification/melting range, as is the case with most other alloy phases. In eutectic solidification one liquid converts into two solids, lamellae of which constitute the eutectic phase. The process starts when constituent A, of the liquid, segregates and solidifies, creating a concentration of constituent B in the nearby liquid. A layer of Liquid B then solidifies, creating a concentration of A, which will solidify as the next layer. The final phase formed is alternating lamellae of A and B.

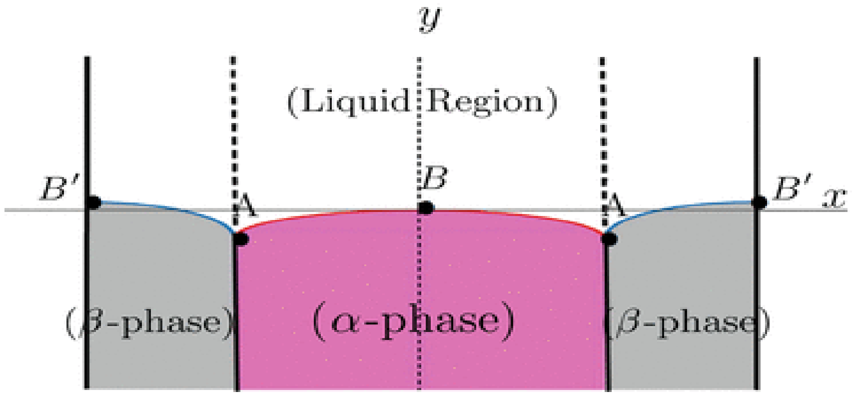

Figure 5 Diagram showing the eutectic lamellar growth front

Gibbs free energy drives the formation of a eutectic phase. In compositions that form eutectic structures, existence of only one of the two components would force that one component to hold an excess of a foreign element. This would increase the strain in the lattice, increasing the Gibbs free energy of the system, taking the structure towards instability. When both components exist together, no excess of one element remains. This lowers Gibbs free energy and leads to stability in the system. Another reason is the balance established between the surface energies of the solid phase and the liquid phase. Due to this, the transformation occurs at a single temperature and results in complete conversion into the alternating solid phase before temperature drops any further.

The size of individual lamellae depends on the cooling rate and influences properties such as thermal stability of the phase. Faster cooling rates produce finer lamellae by further limiting the time available for diffusion in the liquid phase. This makes eutectic phases with finer lamellae more unstable when subjected to thermal treatments such as annealing. Annealing favours diffusion by allowing time for it to occur so fine lamellae readily break. Diffusion occurs, segregation of components is delayed, and coarser lamellae then form. Contrary to the behaviour at high temperatures, finer lamellae provide greater strength at low temperatures.

In comparison to equiaxed grains, lamellar grains have greater strength especially at high temperatures, making alloys with this structure more suitable for high temperature applications. [15]

2.3 Powder Metallurgy

Powder metallurgy is collection of several processing techniques which produce components using powder as the raw material. A major advantage in these techniques is negligible waste produced during product manufacture.

2.3.1 Mechanical Alloying

Mechanical alloying is the process of alloying a mixture of elemental powders in the solid state. Alloying is achieved by milling in a high energy ball mill in a media of steel/ ceramic balls as the grinding media. Powders of various elements are forced to combine due to repeated cold welding, fracturing, and re-welding by collisions with balls and container surface. Moreover, strain and defects created during the process enhance solid state diffusion and further homogenizes the powder [16]

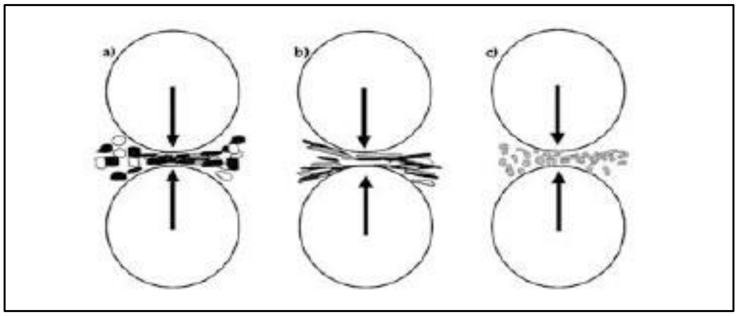

Figure 6 Schematic of the different stages during MA of a nominally ductile powder mixture: a) starting powder; b) flattened, layered composite particles; c) homogenous equiaxed particles

An advantage that mechanical alloying offers over other alloying technique is that of independence of the process with respect to melting points of the elements. When alloying in the molten state, difference in melting points can lead to problems especially if the temperature needs to be increase to a value close to the boiling point of a component. This problem is avoided entirely in the mechanical alloying technique as all components are present only in the solid state.

Commonly, when alloying by this method, one ductile metal is taken to be the binder. Still, there have been many instances of alloying using hard elements only [17]. Along with intermediate phases, super-saturated solid solutions, high entropy alloys, and amorphous alloys, this process has been reported to have produced nanocrystalline phases in many alloy systems.

One of the common problems that are encountered in mechanical alloying is that of contamination. Metal powders are usually processed under an inert gas environment to avoid this, but some sources of contamination are found inside the milling container. It is not unusual for the steel balls, being used as grinding media, to contaminate the mixture with iron atoms. If milling is conducted in a wet medium, it is also possible for the medium to react with the powder, especially at higher temperatures. Moreover, while increasing milling time increases mechanical alloying, it also increasing the probability of the formation of unwanted compounds.

2.3.2 Sintering

Sintering is the process of fusing powder, or a powder compact by application of heat and/ or pressure, without melting the constituents of the powder.

The driving force behind this process is the decrease in surface energy of particles, which is attained through necking and fusion of particles. When kinetic energy is available, atoms move to create a structure of greater stability. As atoms on particle surfaces have high energy and are unstable in comparison to atoms in bulk material, a structure with minimum surface area is desirable. This causes particles to merge during the sintering process.

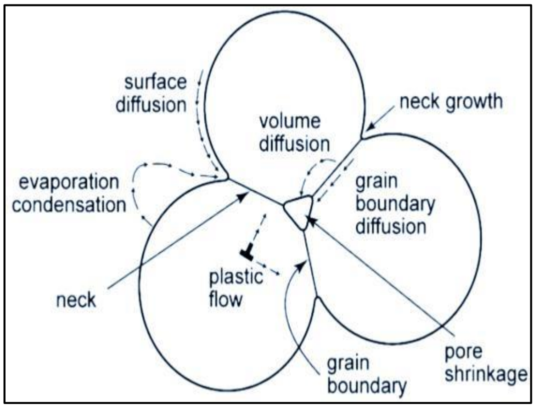

Figure 7 Mechanism of sintering

Sintering involves three steps. In the first step, when the temperature first begins increasing, particles begin to form necks, but complete merger does not occur.

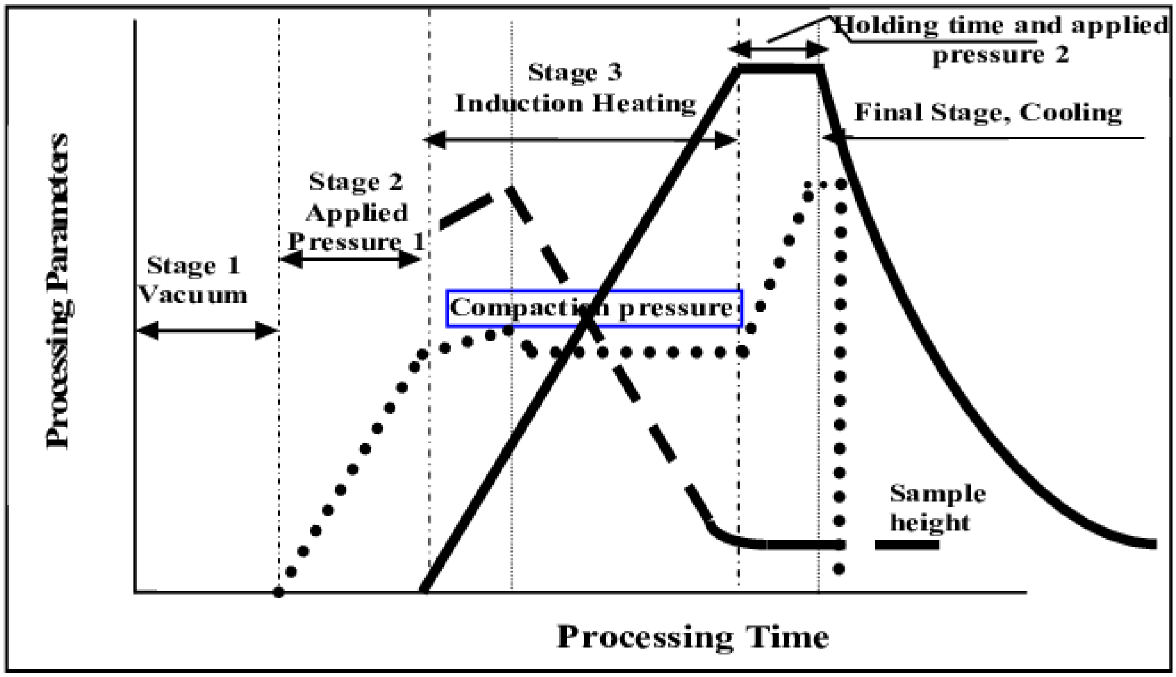

Figure 8 Graph showing a sintering process cycle

In the intermediate step, particle density increases, and most particles have started to merge with each other. Using either a transient liquid phase or a permanent liquid phase, binding among particles is improved, and pores and cracks are filled. In the final stage of sintering, merger is completed, pores disappear, and the material takes the shape of a single solid. Theoretically, sintering would be considered complete when all pores have disappeared, but this is almost never the case.

In fact, low density or high porosity is one of the major problems faced when employing this processing technique. This can be avoided, although, by selecting the correct sintering parameters for that specific material i.e., temperature and time. In some applications such as metal foams and porous ceramic filters, however, high porosity is desirable and is also achieved by controlling the sintering parameters.

2.3.3 Microstructures of HEAs manufactured through PM

In HEAs, the powder metallurgy route results in microstructures that are homogenous, in the form of equiaxed grains. Though at the same time there can be present many brittle phases and inclusions that have precipitated into the matrix. The two main reasons behind these irregularities are contamination and incomplete alloying during the ball milling process. Contamination of oxygen and carbon, and occasionally nitrogen atoms, form carbide, oxide, and nitride secondary phases [18].

Iron contamination from the steel balls used in milling, coupled with incomplete alloying of elements such as Cobalt and Chromium, leave residual metal atoms. These combine to form intermetallic sigma phases of the form Fe-Cr and Co-Cr [19]. It is worth noting that sigma phase will only form when the heating and cooling during sintering is fast enough to restrict sigma diffusion so that this phase can nucleate and grow. The occurrence of laves phase in a consolidated microstructure is also associated with residual metal powder [18]

The formation of two-phase microstructures is favourable in PM route. These dual microstructures are advantageous because they can combine the hardness and ductility of BCC and FCC phases, respectively to give enhanced mechanical properties for applications such as wear resistance. [20]

2.4 Characterization Techniques

2.4.1 Scanning Electron Microscopy

A scanning electron microscope focuses a high-energy electron beam on the material surface. The interaction of the electrons with atoms on, and near the surface gives information regarding morphology and chemical composition of the material. To obtain information regarding morphology, secondary electrons are measured while, to display the contrast with respect to chemical composition, back-scattered electrons are detected. SEM is a non-destructive characterization technique and so, one surface can be analysed several times.

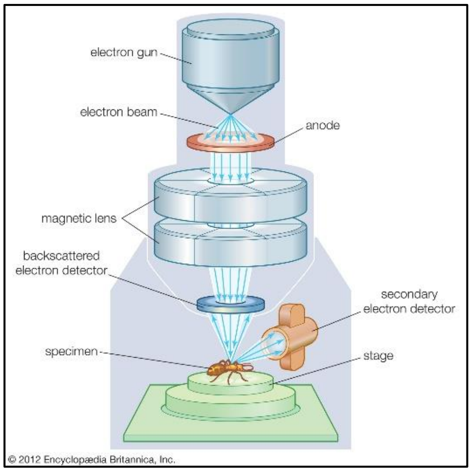

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Figure 9 A scanning electron microscope with secondary and back-scattered electron detectors

This technique can produce images of specimen surface in magnifications up to 30,000x. Present day SEM imaging has the ability to show surface features as small as 1nm. As stated above, secondary electrons are used to give a morphological contrast. When the electron beam interacts with atoms in the surface of the sample, some electrons from the shells of those atoms are knocked out and are detected by secondary electron detectors as shown in figure 8. These form a magnified image of the topography of the sample surface.

Back-scattered electrons are another type of electrons reflected as a result of electron beam and surface atoms interaction. In this case incident electrons collide elastically with nuclei in the surface and are scattered back. Heavier atoms scatter electrons better than lighter atoms. Therefore, more BSEs are detected from regions with heavier atoms and the image formed is brighter. On the other hand, regions with lighter atoms appear darker. So, the contrast in the SEM image is representative of atomic masses of species in the sample.

2.4.2 Energy Dispersive X-ray Spectroscopy

An EDS detector is commonly used alongside SEM to get information about the chemical composition of each phase in the form of atomic percentages.

When electrons from the primary beam are bombarded the sample, some electrons knock out electrons from the shells of surface atoms. When an electron is knocked out from a lower shell, another electron from a higher shell, which is at higher energy, moves to replace the first electron. As a high energy electron occupies a low energy position, excess energy is released in the form of x-rays and these x-rays are detected by the EDS detector. These x-rays are characteristic to every element, so EDS analysis provides quantitative as well as qualitative information about which elements and in what atomic percentages are present.

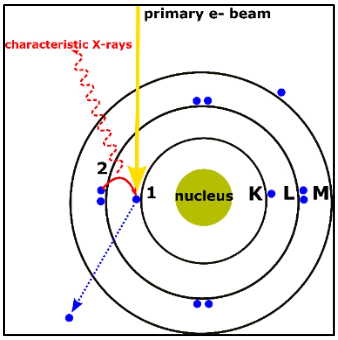

Figure 10 Interaction of a primary electron with an atom's electron, emitting a characteristic X-ray.

While this technique is very useless some limitations also exist. Firstly, EDS is not very sensitive and elements that are present in very low quantities might be measured incorrectly due to the low number of x-rays emitted from their atoms. Secondly, EDS does not work for well for atoms with very low atomic numbers as they do not have enough shells for electrons to jump between them.

Another drawback is that only surface level composition can be measured due to the limited penetrability of electrons. If the material has a different composition in bulk, that will not be detected. Overlap of emitted x-rays and increase in overlap of electron energy levels with increasing thickness also decrease the accuracy of the results [21].

2.4.3 X-ray Diffraction

This characterization technique uses X-ray generated by striking a metal plate with a beam of electrons, to provide information regarding the crystallographic structure of a material. XRD result analysis identifies phases present, and peak shifts are a representation of defects and stresses in the system.

When the generated X-rays are bombarded on to the material surface, they are scattered by the arrays of atoms (crystals), after interaction with electrons of the atoms. The scattering produces spherical waves which, in some specific directions, add up by constructive interference under Bragg's law,

$$n\lambda = 2dsin\theta$$

where λ is the wavelength of the x-ray beam, θ is the incident angle, and d is the spacing between diffraction planes.

The reason that x-rays are able to interact with crystal lattices is that their wavelength is in the same order of magnitude as the spacing between crystal planes, d. The diffracted x-rays are measured by a detector and a graph is plotted, of intensity versus 2θ. Here 2θ degrees is the angle between incoming and outgoing x-ray beams. The relationship between distance between particles and scattering angle is such that smaller particle distances scatter at higher angles. Thus the peaks occur at the right side of an XRD graph.

CHAPTER 3

EXPERIMENTAL PROCEDURES

HEA of NiCoCrNb is prepared by two very different methods, powder metallurgy and electromagnetic levitation. Powder metallurgy uses mechanical alloying technique to form the alloy while EML uses electromagnetic forces to levitate and melt the sample. The experimental procedures involved in our research vary at the beginning of two procedures until the samples are prepared. Afterwards the testing phase for both procedures remains the same.

3.1 Electromagnetic Levitation (EML)

In the Electromagnetic Levitation technique, the sample is placed in a sealed chamber where high vacuum is created using a vacuum pump. Argon was released in the chamber to create an inert environment. The chamber has melted titanium at one side of it and the sample on the other side. The presence of titanium reduces the chance of oxide formation of the sample by oxidizing itself as it has high affinity for the oxygen. The samples used in this technique need to be metallic, as they have to be electrically conductive. The sample was placed in between the copper coils where copper is subjected to high alternating current. The alternating current in the coil causes magnetic fields to develop which induces eddy currents to develop in the material, due to materials resistance it melts. The eddy current melted the sample while the magnetic field levitated the sample. This phenomenon caused the containerless melting. Due to strong eddy currents the melted sample thoroughly mixes due to which segregation of elements is eliminated. Inert gas was propelled on top of the sample to keep it in the middle of the coil. The option of super heating is also available in which the sample is heated to very high temperatures. Due to this, the presence of gases inside the sample or any other contaminants were eliminated. Afterward, the desired melting cycle was achieved through the control of electrical current.

A high speed camera was placed in the chamber to record the melting and solidification of the sample. As stated above, this technique is container less melting and high temperatures are achieved with this technique. So, a pyrometer is used which measures the temperature of the sample using infrared rays, rather than being physically in contact with the sample.

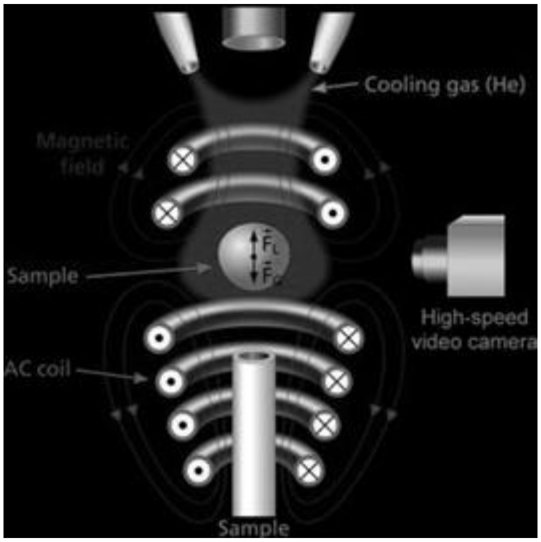

Figure 11 Electromagnetic Levitation

3.2 Powder Metallurgy Route

3.1.1 Ball Milling

Ball milling is commonly used for crushing and grinding of material to a very fine size. In case of powder metallurgy an advanced version of ball milling is used, where alloy making in a ball mill requires high energy and impact which ordinary ball mills cannot do, for this purpose Planetary Ball Mill is used. As the name suggests the containers in a planetary ball mill have 2 circular motions, one around a common center point of the wheel and other is the spinning motion around their own axis similar to the planetary motion of Earth. The spinning motion and rotatory motion of the jars are opposite due to which the balls in the container are set in motion such that they collide with the walls of the container resulting in a powerful impact. These impact forces push atoms of different elements into sites in the crystal structure of other elements resulting in a disordered crystal structure consisting of different atoms at different sites.

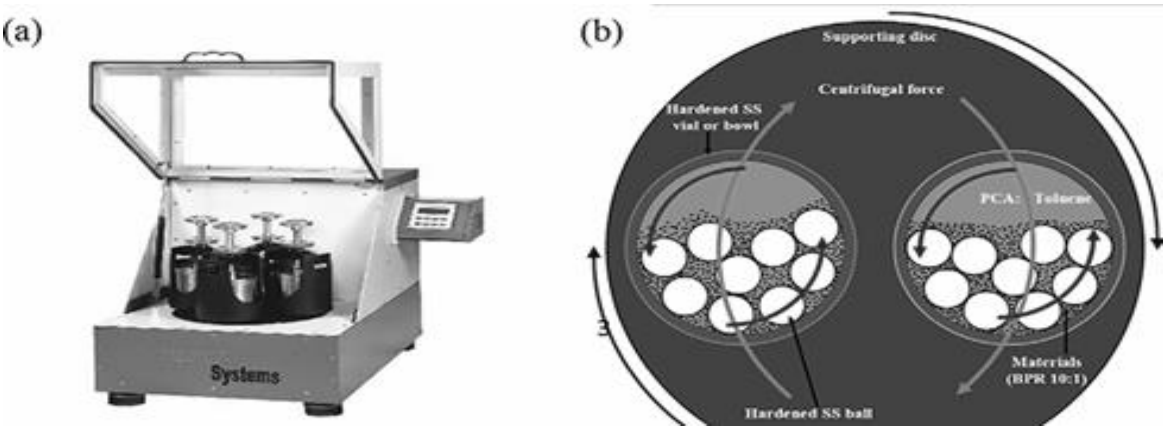

Figure 12 (a) ball mill (b) forces during ballmilling

3.1.1.1 Procedure

The alloy making procedure requires an inert environment such as Helium, Argon or Nitrogen (we used Nitrogen gas environment) to prevent reactions with the atmospheric gases and formation of oxides. The containers are made of stainless steel designed to hold any kind of environment in itself. As for our procedure, the Argon environment is used to avoid oxidation as much as possible. Refractory elements milling action has to be increased. Our parameters of milling are 200 RPM and 28 hours. Time being the only variable here, it was increased from 18hrs so that necessary milling action can take place. The size and ratio of balls used for mechanical alloying has also a great effect on the milling action. 10:1 or 20:1 ball to powder weight ratio is used commonly although 10:1 results in least contaminations. Ball size varies from 3-10 mm in diameter although the majority of the balls used were of 10mm diameter.

3.1.1.2 Milling Time, Environment and Medium

Some metals require less time to diffuse into each other crystal structure because of their coherence and similarity, such metals are mechanically alloyed for a few hours ranging from 6 to 12 hours only. If any refractory element is added then the mechanical alloying process becomes hard as the refractory elements do not diffuse easily. In such cases milling time can be as large as 40hrs.

During the alloying process the metal powder is very vulnerable to oxidation which has to be avoided at all cost. For this purpose, a nitrogen or argon environment is used. Along with oxidation other impurities are also suspected, one of such impurity is carbon. The source of carbon comes from the wet medium during milling. Wet medium is chosen so as to create an ease in the milling action. Ethanol and toluene are 2 liquids used for wet medium but ethanol results in maximum carbon contamination. Toluene on the other hand is preferred in wet mediums for mechanical alloying.

Our High Entropy Alloy consists of NiCoCrNb. These elements are used in powdered elemental form. The powder size is 30-40um. As our HEA has an equimolar ratio of elements in it, all of the elemental powders were added in a weighted amount mentioned below.

3.1.2 Cold Press

Once the high entropy alloy is formed it is in micro powder form which has to be palletized for further processing. For palletization a die and a punch is used such that a hydraulic press applies load over the punch where the powder compresses and forms a pallet. The load applied should not exceed 2 tons as it could crack the pallet and may damage the die itself. During the palletization process the voids and air pockets are reduced to a greater strength which gives the pallet good green strength.

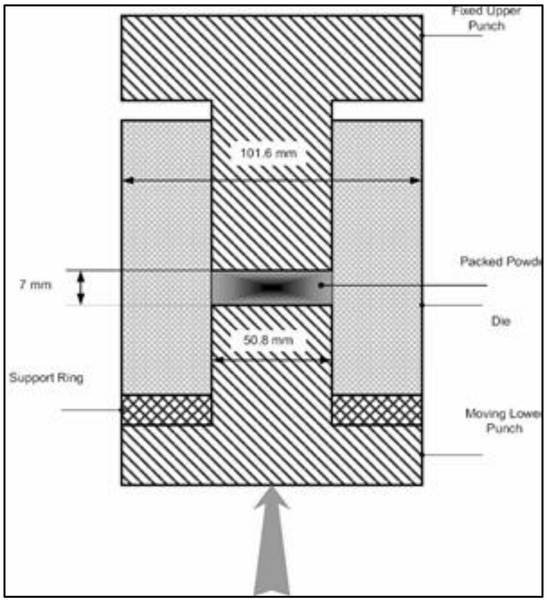

Figure 13 Cold pressing of a sample to form a pellet

Additives are added to the powder to further reduce the voids and air pockets and increase the density of pallets but in our experimental procedure such additives were not used.

3.1.3. Sintering:

Sintering is a process where the powder is heated below their melting point so that the powder particles start to merge together. The merging of particles reduces empty spaces and grains. Process of sintering for metals and nonmetals does not vary a lot, only a few of the parameters are altered. There are a few stages of sintering through which the final solid mass is obtained as seen in Figure 13. It starts by bonding of the particles under heat and pressure, the two particles bond by creating a neck. The necking starts to grow which eliminates the pores and voids among the particles. The elimination of empty space reduces the size of the overall solid and it starts to densify. 100% densification is not feasible although the goal is that the maximum densification is obtained. The process of densification occurs through diffusion which involves various mechanisms like, surface diffusion, volume diffusion, evaporation-condensation, grain boundary diffusion, volume diffusion and plastic flow.

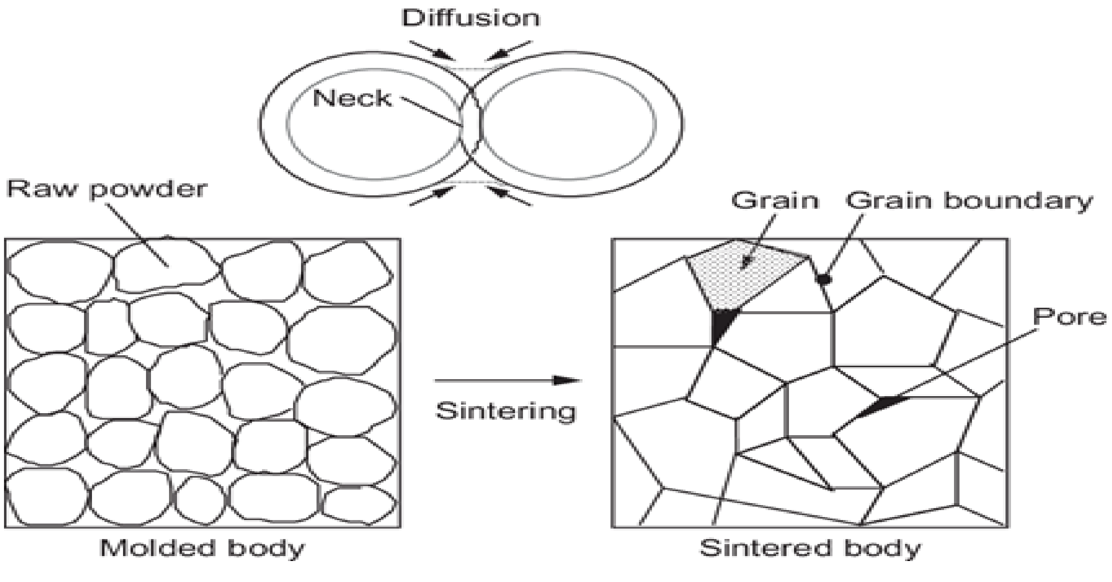

Figure 14 Stages of sintering

3.1.3.1 Process and Parameters:

For sintering of metals, we need an inert environment preferably Argon to avoid oxidation at high temperature. Tube furnace has the capability of providing such an environment. Tube furnace has an alumina tube which is heated by a heating element. Both ends of the tube have flingers attached to it which allows us to generate and hold vacuum or an inert environment. For sintering, the maximum temperature for a material powder is 90% of the melting point. NiCoCrNb has a theoretical melting point of 1833^0C, and its sintering temperature is around 1550^0C. But as we know that the material is mechanically alloyed it has micro and Nano particles which are higher in their energy and thus their melting point reduces. There is no certain way to accurately suggest the melting point of powder. Under these circumstances and considering the capability of the Tube Furnace available 1400C is selected as the sintering temperature of NiCoCrNb.

The Heating cycle has to be gentle as the material goes through densification and shrinkage, the pallet might crack or even break into 2 pieces. For such a reason 1 Hour is required for heating the sample up to the required temperature. The soaking/holding time of the temperature is generally kept 1 Hr but if one requires maximum densification more than 1 Hr can be suggested. Although in our experiment holding time was only 1 Hr. Afterwards the cooling time is kept very slow as the material starts to shrink with the falling temperature. 3-4 hr of cooling time is kept for this experiment. Under an inert environment the presence of oxygen is still there, which causes the material to form a thin layer of oxide over its surface.

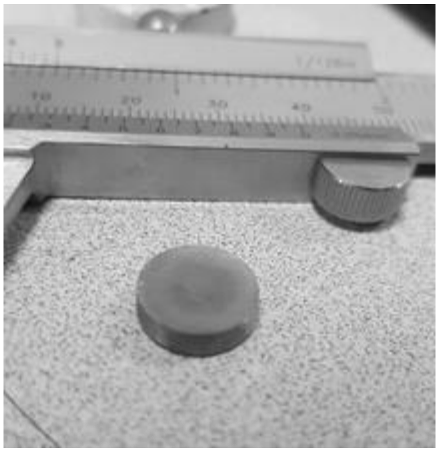

Figure 15 Pellet formed after cold pressing of powder

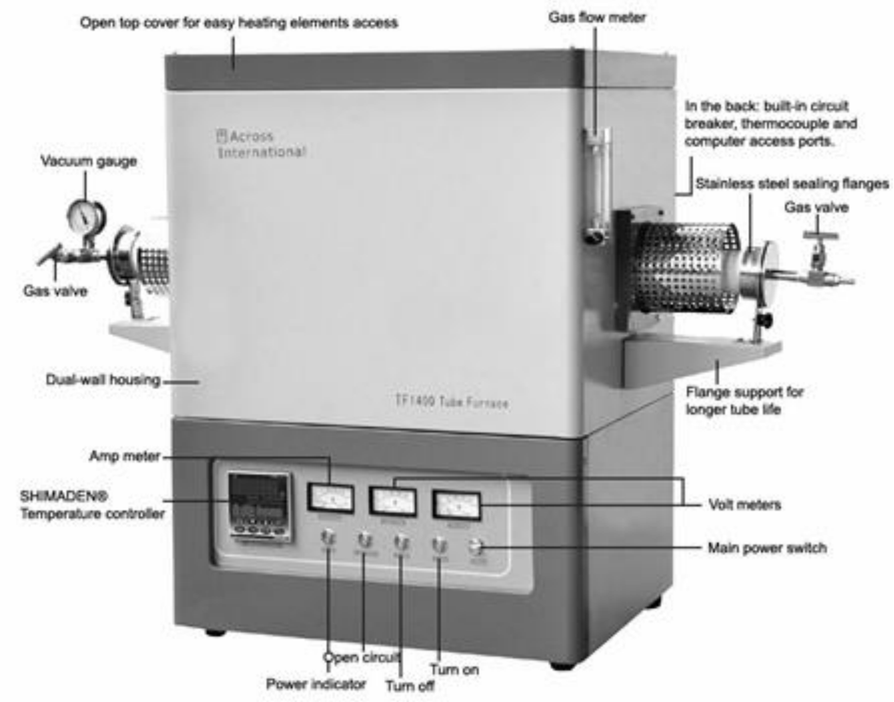

Figure 16 Tube Furnace

3.3 Sample preparation and testing

3.3.1 Grinding and Polishing:

The sintered sample has an oxide layer which is first removed by grinding. Once the golden oxide layer is removed, the sample is mounted in Bakelite powder by hot press. The purpose of mounting is to make the handling of small pallets easy. Now the further grinding involves using sandpaper with the starting grit numbers of 120 till the 2000. The grinding at higher number is carried out till a mirror-like surface is obtained. Once the grinding stage is complete, the sample is polished using alumina slurry containing particles of 0.05 um. The polisher should have

Figure 17 Grinding and polishing of sample

a clean pad free of other contamination or else the sample might get its surface rough. The rpm of the polisher should be kept between 200 – 300 rpm so that handling of the sample is easy and even the surface is polished. After the polishing stage, the sample is etched with nital. The etched sample is ready for micrograph and SEM analysis. Metallurgical microscope is used for micrographing metals by striking light over the sample to be reflected back. The whole process of polishing and grinding was to create a reflective surface so that the light is reflected back to the microscope where the image of the sample's phases can be created.

3.3.2 Scanning Electron Microscope (SEM):

Scanning electron microscopy (SEM) has many functions like Back Scattered Electron (BSE) and Energy dispersive spectroscopy (EDS). BSE provides the image of the sample from within the surface, which provides more detail about the composition. EDS is used to find the composition of elements present in the sample.

After placing the sample, inert gas (argon) is introduced into the chamber. The tip of the gun is polished so that the electron beam is narrow and dispersion of electrons does not occur. The tip of the gun is actually made of tungsten. Once the sample is ready to be scanned, it is placed in a chamber where vacuum is created. Vacuum increases the mean free path of atoms. The atoms keep bouncing off the wall of the chamber but they never go inside the gun chamber nor are they supposed to. This way the electron beam inside the electron gun remains narrow and sharp which provides images of high resolution. 100V is applied to accelerate the electrons. There is a working distance (distance between sample and lens) which changes from sample to sample for better resolution.

3.3.3 Micro Vickers Hardness:

The Microhardness test of the samples were performed on the vickers(HV) scale. The Vickers Hardness test can be performed on any material regardless of the material hardness. It works by applying load on the material to plastically deform it and measure its resistance to the plastic deformation using a standard source. It uses 136 pyramidal diamond indenter to form a square indent, using 1000g or 500g of load. The load was applied for 10 seconds, this time is known as dwell time. Once the indent was created it was then analyzed by a microscope which measures the diagonals of the indent. Through the length of the diagonals the machine measured the hardness of the material.

3.3.4 X-Ray diffraction (XRD):

X-ray diffraction technique is used to determine crystalline structure of a material along with its unit cell and the phases present in it. It works by irradiating x rays on a material and then detecting the intensities of the refracted rays. The X rays are produced by a cathode tube which are filtered to produce monochromatic rays. The monochromatic rays are collimated to concentrate and direct toward the sample. When these rays interact with the material, they are diffracted and detected by a detector. $n\lambda = 2d\sin\theta$ is Bragg's law which relates electromagnetic waves to the lattice spacing and diffracted angle. The material is scanned and all the possible diffracted angles are detected. Through Bragg's law, conversion of electromagnetic rays to the lattice spacing enables us to determine the crystal structure of the material. Every material has a unique lattice spacing. And these unique lattice spacing are matched with the standard reference patterns.

X - Ray diffractometer consists of 3 components. X ray Tube, a sample holder and X-Ray detector. X rays are generated by a cathode tube which heats a metal filament to produce electrons. Voltage is applied to accelerate electrons and concentrate it toward the target material. When the fast moving electrons bombard the target material, characteristic X rays are produced. The target material can be Cu, Fe, Mo or

Cr. To produce monochromatic X - rays coils or crystal monochromators are used. A Goniometer is used to rotate the sample and maintain the angle. The X – rays are bombarded at an angle while the detector is also present at an angle which collects the diffracted ray at 2θ. For a typical material pattern 20° to 80° is selected for a scan.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Scanning Electron Microscopy (SEM):

Scanning electron microscopy (SEM) images for Electromagnetic Levitation and Powder Metallurgy Route at 500x magnification are given in the figures 17, 18 and 19. The SEM images of the Electromagnetic levitation sample shows a dendritic phase with lamellar structure in the interdendritic region (refer to figure 17). These dendrites are rich in Niobium as shown by the bright colour of the phase in the Backscattered Electron SEM image. The inter dendritic region shows the formation of a lamellar phase. The formation of lamellar phase and dendritic phase shows that the HEA is a hyper eutectic alloy. The proeutectic dendritic phase segregates and solidifies first. The remaining melt is at a eutectic composition and thus solidifies into lamellae of Laves and FCC structures.

The figure 18 belongs to the18 hours mechanically-alloyed sample (sintered at 1050°C). The image shows that the sample has very high porosity which is due to incomplete sintering. The grains formed in this alloy are equiaxed.

Figure 19 shows the 28 hours mechanically alloyed sample (sintered at 1100°C). The image shows that porosity has decreased considerably due to proper milling. Complete milling resulted in the formation of the HEA. The image also shows the formation of a dual phased structure, consisting of an FCC and a BCC phase. The white particles that can be seen in the image are inclusions of Niobium Carbide.

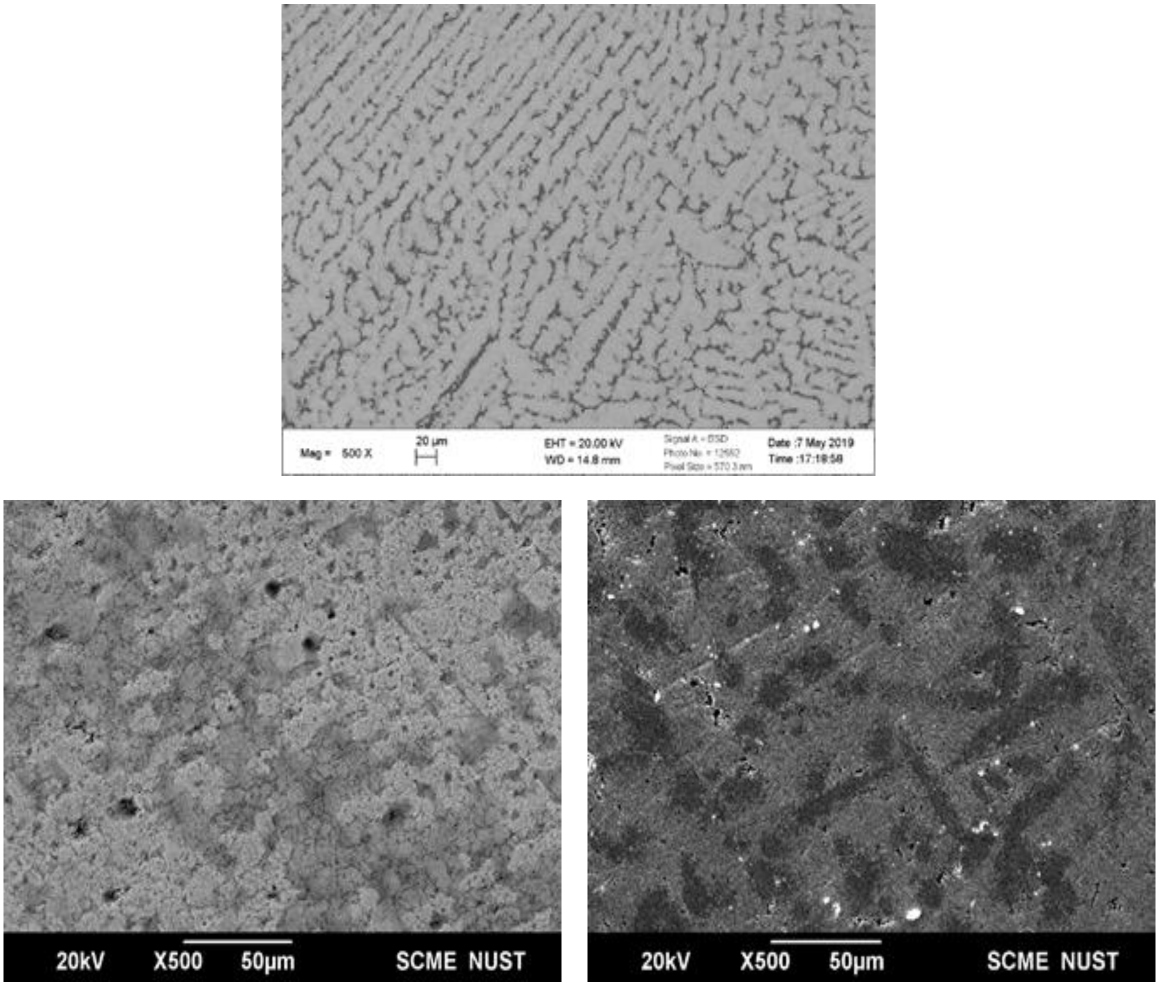

Figure 18 The SEM image of the (a) EML sample, (b) 18-hr milled, 1050C sample, (c) 28-hr milled, 1100C sample.

4.2 EDX- EML:

The EDX results of the EML sample is shown in figure 20 below. The SEM image has been labeled with 2 phases. Phase A is the dendritic phase. A lamellar phase B can be seen in the interdendritic region. The darker lamella is Niobium depleted and can be identified as an FCC phase. The brighter lamella is the Laves phase.

Phase A is lighter in colour showing that a great amount of Niobium, the heaviest element, has dissolved into the Nickel-based FCC solid solution. This is confirmed by the atomic percentage chart where Niobium has the highest percentage of 28.6%.

The darkest fcc phase, visible as a lamella, has the lowest concentration of Niobium. This shows that an appreciable amount of Niobium did not dissolve in the FCC phase and that the phase is a solid solution of Nickel, Chromium and Cobalt.

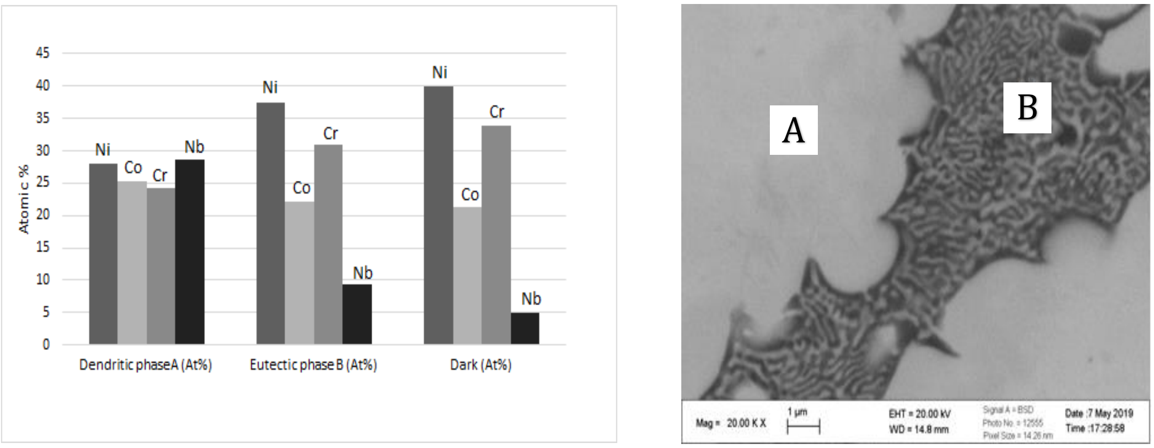

Figure 19 (a) Atomic percentages of elements in phases of the EML alloy, (b) SEM image at 20K magnification.

4.3 Micro Vickers hardness:

All samples were tested on Micro Vickers hardness scale. EML sample showed the highest hardness value among all samples. This is due to its high density and the formation of the intermetallic Laves phase. Laves phase is a HCP structure resulting in high hardness of 800 HV.

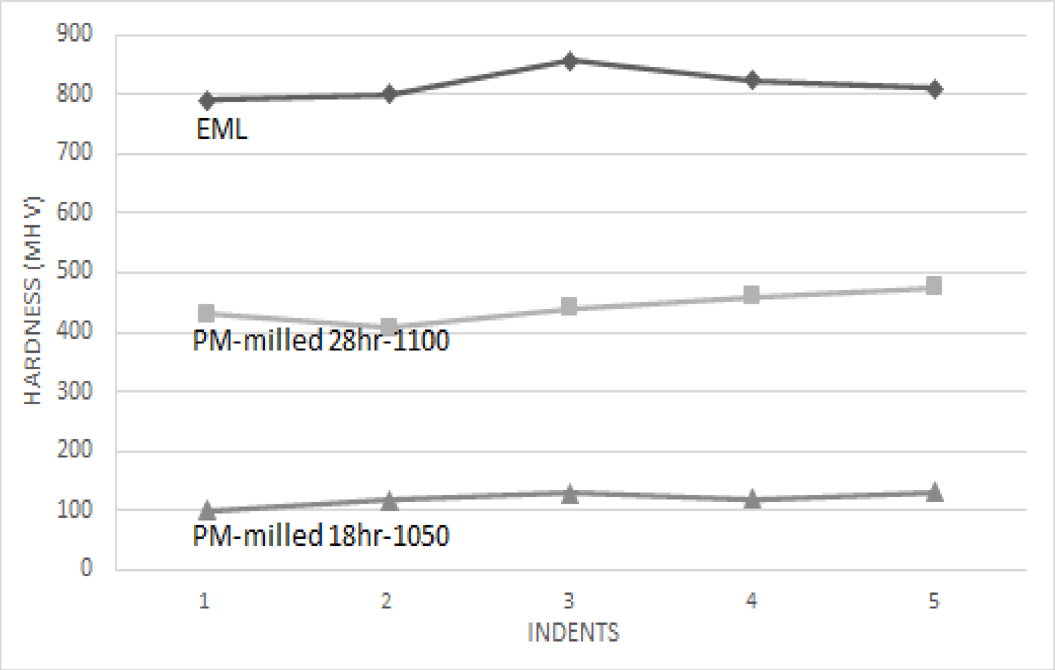

Figure 20 Comparison of micro-hardness values of EML, 18hr-1050C, 28hr-1100C samples

The 18-hours milled, mechanically alloyed sample resulted in the lowest hardness of 120 HV. the low hardness here was due to the high porosity, also because the formation of HEA did not occur in this milling time. The 28-hours milled, mechanically alloyed sample has reduced porosity. Moreover, formation of the BCC phase and the presence of Niobium Carbide resulted in relatively high hardness of 400 HV. This shows that porosity reduction improves the mechanical properties of HEAs. Along with this, having a BCC structure also contributes to the hardness of HEAs. Sintering temperature also seemed to greatly affect the porosity of the powdered sample. If proper sintering takes place then the mechanical properties improve.

4.4 X Ray Diffraction (XRD):

The XRD of the Electromagnetic Levitation (EML) and Powder Metallurgy route sample are shown in the figure 23. The EML sample XRD pattern shows the formation of the Laves phase which has the composition of Co2Nb. In our research, the XRD of the EML sample showed peaks of the laves phase. Laves phase has HCP structure and its peaks are highlighted by red dots. Along with the laves phase we can also see the yellow dotted peaks denoting the FCC structure. In our EML sample FCC structure consists of a Nickel-based solid solution. The Nickel-based solid solution contains Nb, Co and Cr which produces lattice strain. This lattice strain sometimes creates a peak shift in the XRD pattern but in our case peak shifting did not occur.

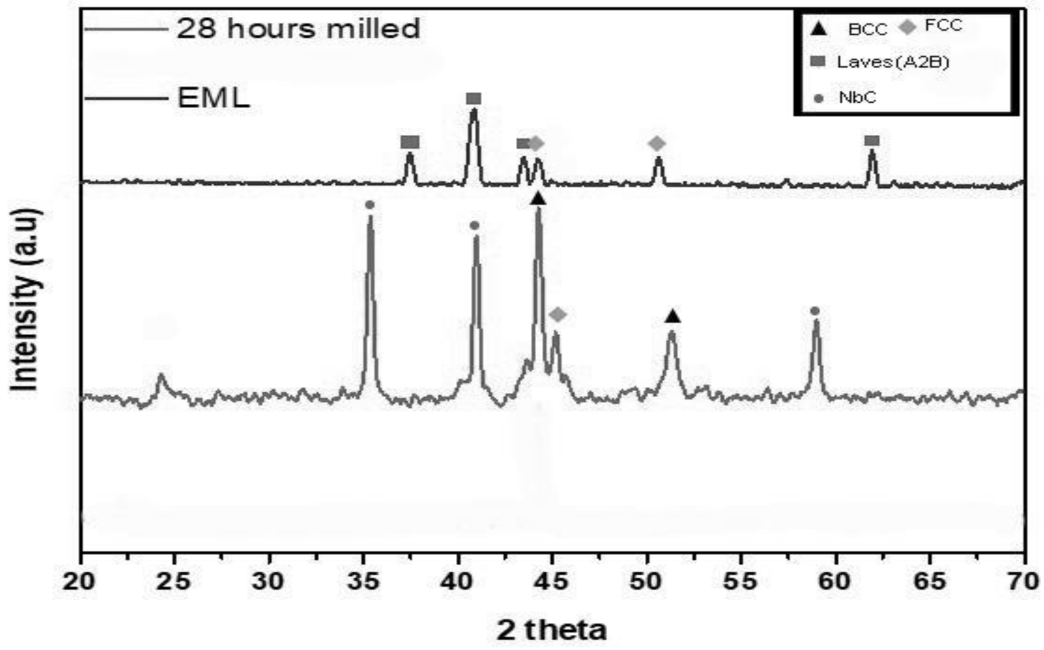

Figure 21 XRD peaks of EML and 28hr-1100C samples

The Powder Metallurgy Route sample was milled for 28 hours in a high energy planetary ball mill which was sintered at 1100°C for 1 hour. Our mechanical alloying was done in wet milling media containing toluene. Toluene being an organic compound is rich in Carbon and can be a source of contamination. If we look at our milled sample XRD pattern we can see that green dotted peaks show the formation of Niobium Carbide (NbC). NbC has been reported to be formed in HEAs due to the contamination of milling jars and milling media. In our sample milling media sourced the sufficient carbon for the formation of Niobium Carbide.

Some metals have high affinity for Niobium while others have relatively less. Due to this reason Niobium made 2 solid solutions with Chromium and Nickel. As Niobium is a BCC structured metal and Chromium also has a BCC crystal structure,it can easily dissolve Niobium in its crystal structure as compared to Nickel which is FCC structured. Due to this reason the XRD pattern showed the formation of BCC structure which consists of Chromium solid solution. Nickel being a FCC structure also made a solid solution which can be confirmed by FCC peaks from the XRD Pattern.

4.5 Discussion:

Electromagnetic Levitation route results in HEA containing Laves phase and FCC phase. The alloy formed has the maximum possible density which is one of the factors which give improved mechanical properties in comparison to the powder metallurgy route, where full density is rarely achievable. The internal mixing of the metals due to the Lorentz forces created by the eddy current causes thorough mixing of the sample thus removing any chance of segregation. This method helps form a dendritic structure which surrounds an interdendritic region which consists of a lamellar structure with lamellae of FCC and Laves phases. This gives the sample a high hardness that is 800HV due to an ideal amount of the ductile phase, that is FCC, and a high hardness phase that is Laves phase. The presence of Laves phase and high density contributed to the alloys' high hardness values which resulted in making the HEA suitable for extreme applications which require high strength.

The mechanically alloyed sample has improved its hardness by changing its procedural parameter. This showed the significance of the processing parameters when using the powder metallurgy route. The 18 hour milled sample resulted in poor mechanical properties due to incomplete sintering and proving that the HEA had not been formed. This powder was sintered at 1050°C which was sufficient for proper sintering yet, the alloy showed extremely low hardness values for an HEA and a highly porous structure as can be seen in the SEM images (Fig.).

When the metallic powder was milled further for 10 more hours, making a total of 28 hours milling time, the XRD results showed the formation of dual phases .i.e. FCC and

BCC phase. The BCC being a harder phase contributed to the improvement of mechanical properties. Sintering temperature was increased to 1100°C which resulted in better density and reduced porosity. The reduction of porosity also had an positive effect on the mechanical properties of the HEA. The formation of HEA containing FCC and BCC phase after 28 hours of milling improved its hardness value by 300 HV thus, giving a resultant hardness value of 430HV. Another factor to be considered for improved mechanical property was the formation of niobium carbide in the structure as can be seen in the XRD results in (fig.). Niobium Carbide being a hard ceramic inclusion affects the hardness of our HEA.

We can infer that with further research and improved processing parameters such as sintering temperature, sintering time, or milling time of the metallic powders, the properties of the NiCoCrNb HEA can be further improved.

CONCLUSION

In our study both processing routes, Electromagnetic Levitation and Powder Metallurgy, were successful in the development of the high entropy alloy NiCoCrNb as shown by our XRD results. The routes give solid solutions with intermetallic phases and carbides respectively, each component adding hardness to the respective alloy.

The 18-hrs milling time was insufficient for the formation of high entropy alloy as could be observed by the extremely low microhardness values but increasing the milling time to 28hrs produced better results. The 18hrs sample was sintered at 1050°C which resulted in a low density and porous sample but increasing the sintering temperature and milling time to 1100°C and 28 hours respectively improved the densification of the sample and decreased the amount of porosity even though the sintering time was kept constant at 1hr. These changes in parameters for the 28hr-1100°C sample showed noticeable improvement in the mechanical properties. The increase in hardness was also credited to the formation of HEA in the 28hr-1100°C sample as well as the formation of Niobium Carbide in the structure.

The electromagnetic levitation process resulted in the formation of eutectic lamellar microstructure while the powder metallurgy route resulted in two-phase microstructure with NbC inclusions. The EML sample resulted in superior hardness at around 800 HV than the samples created through powder metallurgy. The powder metallurgy route showed promise of betterment in the properties of the alloy with further changes in processing parameters as can be seen with slight change in processing parameters the alloy improved hardness from 120 HV to 400HV.

The processing routes and the processing parameters thus showed a huge effect on the microstructure of the resulting alloy as well as the mechanical properties of the high entropy alloy formed. Powder metallurgy route also shows promise in further improving the properties through the addition of ceramic or other additives to the metal powder mixture, like Niobium Carbide in our case.

An advantage of the powder metallurgy over Electromagnetic Levitation is the potential for it to be commercialized. Alloys parts can be manufactured in bulk while in comparison EML can only be used in research. Powder metallurgy also offers a wider range of possible shapes and sizes for production of parts. Through this route, complex shapes can be manufactured while avoiding problems such as compositional inhomogeneity, alloy segregation, and shrinkage which are common during casting. The powder metallurgy process is more energy efficient. Melting is not required so even refractory elements can be processed at relatively low temperatures. The process parameters can be used to greatly control the microstructure and properties that we need in our alloy.

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