# Phase Equilibria Study and Mechanical Properties of Multicomponent Alloys

Ph. D. Thesis

By SANDEEP JAIN

(1701205006)



## DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE

## INDIAN INSTITUTE OF TECHNOLOGY INDORE NOVEMBER 2022

# Phase Equilibria Study and Mechanical Properties of Multicomponent Alloys

## A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

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*by* SANDEEP JAIN (1701205006)



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# **INDIAN INSTITUTE OF TECHNOLOGY**

### INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "PHASE EQUILIBRIA STUDY AND MECHANICAL PROPERTIES OF MULTICOMPONENT ALLOYS" in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF METALLURGICAL OF ENGINEERING SCIENCE, INDIAN INSTITUTE AND MATERIALS TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from December 2017 to November 2022 under the supervision of Dr. Sumanta Samal (Associate Professor) & Dr. Vinod Kumar (Associate professor) at Department of Metallurgical Engineering and Material Science (MEMS) Indian Institute of Technology (IIT) Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

> Sondeeter 50105123 Signature of the student with date (SANDEEP JAIN)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of Thesis Supervisor#1 with date

(Dr. SUMANTA SAMAL)

Signature of Thesis Supervisor#2 with date (Dr. VINOD KUMAR)

SANDEEP JAIN has successfully given his Ph.D. Oral Examination held on 29 May 2023.

S. Same 2905 2023 Signature of Thesis Supervisor #1 with date

(Dr. SUMANTA SAMAL)

Signature of Thesis Supervisor #2 with date

(Dr. VINOD KUMAR)

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Sandeepsin SANDEEP JAIN

# **DEDICATED TO**

# MY FAMILY

# MY WELL-WISHERS

MÝ JAINISM & MÝ NA TION

### Abstract

Multicomponent alloys have been attracting attention worldwide and constitute an active, frontier area of research in the exploration of novel materials development. The current thesis focuses to design and development of multicomponent alloys Al-Ni-X (X = Fe, Cr, Co, V, Ta, Si ), Al-Cu-X (X = Si, Ni), Single phase Fe-Co-Ni-Cr-V-X (X = 0, Al) HEAs and Fe-Co-Ni-Cr-V-Al-Ta<sub>X</sub> (X = 2.5%, 5%, 7.5% and 10%) EHEAs to establish new phase equilibria using integrated approach by combining thermodynamic simulation, numerical simulation and experimental solidification techniques for the development of novel materials for better mechanical properties and high temperature applications. A numerical simulation model is successfully developed for vacuum arc melting cum suction casting unit by using ANSYS Fluent software and validated in a well manner. Experimentally, it is found that the microstructure of studied multicomponent alloys consist of FCC solid solution phase and one or more intermetallic phases. The mechanical properties of multicomponent alloys are carried out at room temperature as well as at elevated temperatures. It is to be noted that high strength and plasticity are attributed to the synergic effects of eutectics of different morphologies.

Firstly, the effects of different alloying elements (Fe, Cr, Co, V, Ta, Si, Cu) are evaluated on Al-Ni and Al-Cu system. (i) For Al<sub>98.6</sub>Ni<sub>0.5</sub>Fe<sub>0.9</sub> ternary alloy, the invariant quasiperitectic reaction, i.e.,  $L \rightarrow Al_9FeNi \rightarrow$ (Al)<sub>ss</sub> + Al<sub>3</sub>Fe, has been proposed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 234 MPa, 16.7% and 93.5 HV. (ii) For Al<sub>92</sub>Ni<sub>4</sub>Cr<sub>4</sub> ternary alloy, the invariant ternary eutectic reaction (i.e.,  $L \rightarrow (Al)_{ss} + Al_3Ni + Al_7Cr$ ) is observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 190 MPa, 10.5% and 74.6 HV. (iii) For Al<sub>92</sub>Ni<sub>4</sub>Co<sub>4</sub> ternary alloy, two dendrite (Al)<sub>ss</sub> and Al<sub>8</sub>(Co, Ni)<sub>2</sub> phases with a binary eutectic reaction (L  $\rightarrow$  Al<sub>ss</sub> + Al<sub>3</sub>Ni) are

observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 253 MPa, 14.5% and 96.8 HV. (iv) For Al<sub>93</sub>Ni<sub>4</sub>V<sub>3</sub> ternary alloy, three dendritic phases of (Al)<sub>ss</sub>, Al<sub>3</sub>V and Al<sub>3</sub>Ni and one ternary eutectic (L  $\rightarrow$  Al<sub>ss</sub> + Al<sub>3</sub>Ni+ Al<sub>3</sub>V) reaction are observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 259 MPa, 16.5% and 100.97 HV. (v) For Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> ternary alloy, five dendritic phases of (Al)<sub>ss</sub>, Al<sub>3</sub>Ni<sub>2</sub>, Al<sub>7</sub>Ni<sub>3</sub>, Al<sub>3</sub>Ta and Al<sub>5</sub>Ta<sub>3</sub>Ni<sub>2</sub> are observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 296 MPa, 18% and 284.74 HV. (vi) For Al<sub>84</sub>Ni<sub>4</sub>Si<sub>12</sub> ternary alloy, two dendritic phases of (Al)<sub>ss</sub> and Al<sub>3</sub>Ni, one binary eutectic (L  $\rightarrow$  Al<sub>ss</sub> + Al<sub>3</sub>Si) reaction and one ternary eutectic (L  $\rightarrow$  $Al_{ss} + Al_3Si + Al_3Ni$ ) reaction are observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 201 MPa, 14% and 80HV. (vii) For Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> ternary alloy, the invariant quasiperitectic reaction i.e., L+Al<sub>7</sub>Cu<sub>4</sub>Ni  $\rightarrow \alpha$ -Al+ Al<sub>2</sub>Cu is proposed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 336 MPa, 4.29% and 188.84 HV. (viii) For Al<sub>85</sub>Cu<sub>10</sub>Si<sub>5</sub> ternary alloy, a combination of binary (L  $\rightarrow \alpha$ -Al + Al<sub>2</sub>Cu) and ternary eutectic (L  $\rightarrow \alpha$ -Al + Al<sub>2</sub>Cu+  $\beta$ -Si) reactions has been observed and the mechanical properties (UTS, % Elongation and Microhardness) of the alloy are 287.7 MPa, 6.22% and 181.67 HV. The developed ternary multicomponent alloys exhibit improvement in strength and ductility, which can be considered as potential candidates for low temperature applications due to thermal stability upto eutectic temperature around (660 °C). However, the strength can further be enhanced further using similar microstructural design consisting of FCC solid solution phase or combination of FCC solid solution phase and one or more intermetallics as obtained in multicomponent ternary alloys using similar elements as major principal elements which is knows as multicomponent concentrated alloys or popularly known as high entropy alloys (HEAs).

Secondly, single FCC phase Fe-Co-Ni-Cr-V-X (X = 0, Al) HEAs have been designed and developed which shows the formation of single FCC phase. A HEA with the best mechanical properties (UTS ~519 MPa, % Elongation ~64.84% and Microhardness ~258.73 HV is selected for investigation of hot deformation behaviour. The hot deformation behaviour at different temperatures (1073 K to 1323 K) and different strain rates ( $10^{-3}$ s<sup>-1</sup> to 1 s<sup>-1</sup>) are carried out. The deformation behaviour has been correlated with the grain size distribution and dislocation movements with the help of EBSD analysis. The optimum thermomechanical processing conditions of single-phase Fe<sub>20</sub>Co<sub>25</sub>Ni<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub> FCC HEA lie in the temperature range 1150 K-1350 K and strain rate range  $10^{-1}$  s<sup>-1</sup> to 1 s<sup>-1</sup>.

Finally, Fe-Co-Ni-Cr-V-Al-Ta<sub>X</sub> (X = 2.5%, 5%,7.5% and 10%) EHEAs have been designed and developed which shows the formation of (FCC + Intermetallic) microstructure with better mechanical properties (UTS ~1257 MPa, % Elongation ~28.5% and Microhardness ~651.4 HV) and the mechanical behaviour of the EHEAs has been correlated with the help of numerical simulation results. It is observed that the EHEAs having (FCC + Intermetallic) microstructures show the better mechanical properties (UTS ~1257 MPa, % Elongation ~28.5% and Microhardness ~651.4 HV) compared to the developed ternary alloys (UTS ~296 MPa, % Elongation ~18% and Microhardness ~284.74 HV).

### **LIST OF PUBLICATIONS**

#### List of published papers from thesis work

- Sandeep Jain, R. Jain, M. R. Rahul, S. Samal, V. Kumar, "Phase Equilibria and Mechanical Properties in Multicomponent Al–Ni–X (X = Fe, Cr) Alloys" Transactions of the Indian Institute of Metals, 2018, 71 (11), 2819–2825. DOI: 10.1007/s12666-018-1420-y.
- Sandeep Jain, Piyush Kumar, Abhijit Ghosh, Vinod Kumar, Sumanta Samal, "Solidification simulation of single-phase Fe-Co-Cr-Ni-V high entropy alloy" Philosophical Magazine, 2022, 102 (18), 1832-1852. DOI: 10.1080/14786435.2022.2084793
- Sandeep Jain, Mahesh Patel, Sumanta Samal, Vinod Kumar, "Effect of Si on microstructure and mechanical properties of Al-Cu alloys" Silicon, 2023. DOI: 10.1007/s12633-022-02131-6
- Sandeep Jain, Naveen L, Vinod Kumar, Sumanta Samal, "Solidification simulation and experimental validation of 6 component single-phase high entropy alloy", Transactions of the Indian Institute of Metals, 2023. <u>DOI: 10.1007/s12666-022-02821-0</u>.
- Sandeep Jain, Vinod Kumar, Sumanta Samal, "Effect of Ni and Si alloying elements on the phase evolution and mechanical properties of Al-Cu alloys" Materials Physics and Chemistry, 2023. DOI: 10.1016/j.matchemphys.2023.127421

#### List of an ongoing manuscript from thesis work

 <u>Sandeep Jain</u>, Vinod Kumar, Sumanta Samal, "Effect of Ta on the evolution of phases and mechanical properties of novel seven components Fe-Co-Ni-Cr-V-Al-Ta eutectic high entropy alloys: Experimental study and Numerical Simulation" The Transactions of Indian National Academy of Engineering, 2023 (Under Review).

- Sandeep Jain, Vinod Kumar, Sumanta Samal, "Prediction the effect of Ta on the mechanical behaviour and experimental validation of novel six components Fe-Co-Ni-Cr-V-Ta eutectic high entropy alloys" Refractory Metals and Hard Materials, 2023 (Under Review).
- Sandeep Jain, Vinod Kumar, Sumanta Samal, "Microstructural evolution and mechanical behaviour of Al-Ni-X (X = Fe, Cr, Co, V, Ta and V) ternary alloys" Materials Characterization, 2023 (Under Review).
- Sandeep Jain, Rama Krushna Sabat, Vinod Kumar, Sumanta Samal, "Design and deformation Characteristics using EBSD analysis of 6 component single-phase high entropy alloy" (Ready for Submission).
- Sandeep Jain, Reliance Jain, M R Rahul, Vinod Kumar, Sumanta Samal, "Hot Deformation behaviour of 6 component single-phase high entropy alloy" (Under Preparation).
- Sandeep Jain, Reliance Jain, Vinod Kumar, Sumanta Samal, "Review on the development of high strength eutectic high entropy alloys for high temperature applications" (Under Preparation).

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## **ACRONYMS**

HEAs	High Entropy Alloys					
EHEAs	Eutectic High Entropy Alloys					
XRD	X-Ray Diffraction					
SEM	Scanning Electron Microscopy					
TEM	Transmission Electron Microscopy					
EBSD	Electron Back Scattered Diffraction					
BSE	Back Scattered Electron					
EDS	Energy Dispersive X-Ray Spectroscopy					
ANN	Artificial Neural Network					
DRV	Dynamic Recovery					
DRX	Dynamic Recrystallization					
CALPHAD	CALculation of PHAse Diagrams					
FEM	Finite Element Method					
DMM	Dynamics Materials Modelling					
YS	Yield Strength					
UTS	Ultimate Tensile strength					
LAGBs	Low Angle Grain Boundaries					
HAGBs	High Angle Grain Boundaries					

### **Chapter 1**

### **Introduction and Literature survey**

#### **1.1 Introduction**

Energy is the most important requirement for survival on a global scale. The types of machinery and equipment have a significant impact on power output which are used to generate power, such as gas turbines and jet engines. The power generation business is primarily operated at high working temperatures, which serves to improve the industry's overall efficiency. The latest equipment is advanced, and it is made of high-strength materials. The great strength comprises exceptional specific strength, creep resistance etc. both at room temperature and at elevated temperatures. Several studies revealed a scientific method for designing equipment and its components for a longer life cycle in a high-risk working environment. Since then, the demand for such materials has sparked a revolution in materials science and engineering, which stems from numerous recent discoveries. It usually starts with one or two basic components and then adds extra elements (alloying elements) to acquire the desired properties.

Since ancient times, the path from pure metal to alloys has played an important role in the development of new metallic materials. In recent time, aluminium and aluminium alloys are widely used in automobile and aerospace engineering due to the light weight component. Aluminium alloys are widely used due to their excellent properties like good strength weight ratio, good malleability, high machinability and workability etc. A wide range of industries, including the automotive, aerospace, construction, and marine sectors, have increased the use of aluminium alloys. **Fig.1.1** depicts the increase the use of aluminium alloys in the automotive industry in every year; the prediction for 2025 is more than 500 lbs of aluminium per vehicle[1].



**Fig.1.1** Increment in the uses of Al alloy in automotive industries over half a century [1]

Most traditional aluminium cast alloys are based on the excellently castable Al-Si eutectic system. The fundamental problem, however, is that the Al-Si eutectic has a low solidus temperature, which results in poor high-temperature mechanical properties. Therefore, efforts were made to substitute Al-Si based eutectic alloys [2]. Wang et al. [3] optimised the Cu, Fe, and Mn contents to produce Al-Si-Cu-Fe-Mn eutectic alloys with improved mechanical properties. One of the most important candidates in Al based alloys is Al-Ni system. With the addition of 6.1 % Ni, Al<sub>3</sub>Ni phase formation takes place which create a coherence interface with FCC Al solid solution phase and maximize the strengthening capability of the alloy [4].

Despite significant advancements, there is still a need to raise the stressstrain curve of Al alloys to higher values for applications involving static and dynamic situations as well as high temperatures. In addition, with the growing market for electric vehicles (EVs), high modulus aluminium alloys will be required to sustain the significant mass of the vehicle.

By considering the wide range of applications for Al alloys, there is market demand for further enhancements to Al's mechanical properties, such as modulus values, particularly at higher temperatures. As the twenty-first century began, a new class of alloys known as High-Entropy Alloys (HEAs) was found to fulfil this demand [5]. HEAs, which have the potential to gain superior mechanical properties and simple castability, have recently attracted the interest of researchers because of their significant advantages over conventional alloys for various applications. Experimentally, the multicomponent HEAs usually reveal a simple microstructure composed of solid solutions of the FCC and/or BCC phases. This is believed to be the outcome of alloying various elements in an equiatomic or nearly equiatomic ratio.

In order to achieve mechanical properties, EHEAs are designed using an in-situ microstructure that combines the advantages of intermetallics and solid solution phase(s) [6]. It is necessary to develop higher-order multicomponent EHEAs in order to predict a slow diffusion. As a result, solidification processing techniques used in the bulk preparation of EHEAs with ultrafine microstructure will probably provide EHEAs with improved mechanical properties for large-scale applications. The research community has recently made commendable efforts to develop novel HEAs by carefully choosing elements, composition and heat treatments that have excellent properties like a combination of strength and plasticity, high hardness, wear resistance etc [7–9]. As a result, it is anticipated that the field of EHEAs will continue to be active for researchers in the near future and inspire hope for the development of materials with superior properties for high-temperature applications.

Numerical modelling is necessary to understand the behaviour and performance of the systems due to the complex nature of the phase change mechanism during the melting and solidification process. To solve the phase transition problem in various geometries, several numerical models have been created over the years. Phase change processes in spherical, rectangular, and cylindrical geometries have been thoroughly modelled using fluent CFD software. A system can be optimised for a specific application by using the commercial Fluent package, which will reduce the amount of required modelling efforts. Therefore, to obtain the superior properties of the desired alloy, it is important to study the solidification process for a specific casting method. The solidification simulations are an effective tool for investigating the solidification process by depicting the solidification at different points during the casting process.

# **1.2 Development of Al based multicomponent alloys (Low entropy alloys)**

#### 1.2.1 Necessity of multicomponent alloys

From several centuries, metallurgist and material scientists have been motivated to develop new materials which can be lighter, ductile and stronger compared to the existing material at room temperature and at elevated temperature [10]. The basic need to achieve these properties are to develop multi component alloys. Alloying is the greatest gift to humankind because by adding the alloying elements, the properties of the material can be altered. Multicomponent alloys have been attracting the attention of researchers to explore the research to develop a novel material. Low entropy alloys and high entropy alloys can be defined in the development of multicomponent alloys.

In the present scenario, material community has been increasing attention to develop light weight material that possess good strengthdensity ratio with excellent performance at room temperature and at elevated temperature [11]. Alloys containing Al as a principal element are the potential candidates for replacing the heavier materials like cast iron, steel etc in many engineering applications due to their outstanding properties like low density, high specific strength, good machinability, excellent formability etc [12]. By replacing the Cast Iron with Al alloys can reduce the weight of the engine components by 30-60% and enhance the fuel efficiency by 10- 15% [13] Al alloys have a good stiffness to weight ratio in all metals and alloys as shown in **Fig. 1.2**.

# **1.2.2 Design Methodology to develop the Al based multicomponent alloys**

The development of Al alloys may be accomplished via eutectic solidification of hard intermetallic phases with the in-situ reinforcement in the metal matrix, where coupled growth of two or more phases happens simultaneously [14]. Among the binary eutectics, Al-Al<sub>3</sub>Fe, Al-Al<sub>2</sub>Cu, and Al-Al<sub>3</sub>Ni have received the greatest attention. In the

eutectics Al-Al<sub>3</sub>Fe and Al-Al<sub>3</sub>Ni, rod-shaped intermetallic phase fibres are incorporated into the Al matrix [15, 16]. Contrarily, the growth morphologies for Al-Al<sub>2</sub>Cu eutectic are distinctive and include an additional Al<sub>2</sub>Cu lamella in Al matrix. These eutectics have strong intermetallic phases that hinder the dislocation motion and hence increase strength, that's why they have good mechanical properties [17]. However, the ductility of the alloys is frequently compromised by the high-volume fraction of intermetallic phases.

The interlayer spacing, phase fraction, and morphology etc influence the properties of the eutectics. Recent research has shown that carefully altering the microstructure through ternary addition or rapid solidification can increase strength and plasticity [18–20]. The morphology of the binary eutectic can be altered by a slight ternary element addition.

Bulk ultrafine eutectic alloy with micron-scale dendritic phases has recently been reported to be a promising material with the improved and well-balanced combination of mechanical properties needed for advanced applications.



Fig 1.2 Comparison of Al alloys with other metals and alloys

## **1.2.3 Mechanical Properties enhancement mechanism of Al based** multicomponent alloys

Due to above mentioned properties, Al-based alloys are a possible contender for structural application and they have gained a lot of attention from the researchers throughout the world [21, 22]. However, the yield strength of these alloys is very less compared to steel which constrains their applications for room temperature and elevated temperature [23]. Therefore, one of the major challenges that are limiting the wider application of Al based alloys is the inherent poor mechanical properties at room temperature and at elevated temperatures. In order to improve the properties of the alloys, it is crucial to find a suitable strengthening method. As a result, numerous efforts have been made to develop new Al-based alloys to enhance their mechanical properties [11, 21, 24]. The design strategy to develop novel Al-based alloys with improved mechanical properties is either by modification in microstructure with the inclusion of alloying elements [25–29] or by selecting the proper processing route [30, 31].

#### (i) Modification in microstructure for strengthening of alloys

In the phase diagrams, the term "eutectic" refers to the presence of minima in the liquidus curve which is discovered by Guthrie in 1884 [32]. The eutectic alloys have been extracted more attention by the research community and developed as an advanced material in multicomponent alloys like binary alloys, ternary alloy, and so on. They are getting more attention due to their superior properties compared to single crystal or single-phase alloys [33]. Depending on the cooling rate, several different forms of microstructures can be seen in the eutectic alloy [34, 35]. Mechanical properties of the eutectic alloys which contain lamellar microstructure are superior due to the presence of soft solid solution and hard intermetallic phase [36–38]. By adding the amorphous phases or nanoquasi crystalline phase with the solid solution phase is also a good method to achieve the high strength Al based amorphous alloys [39]. By controlling the composition, clustered atomic configuration and stability of supercooled liquid by the rapid

solidification and powder metallurgy techniques, high-strength Albased bulk alloys containing nanoscale nonperiodic phases were produced. The nonperiodic phases are composed of an amorphous or an icosahedral quasicrystalline phase. In particular, the Al-based bulk alloys consisting of nanoscale icosahedral particles surrounded by FCC-Al phase exhibit much better mechanical properties exceedingly largely those for the commercial high strength type Al-based alloys [40]. Akihisa Inoue et. al has been reported that amorphous metallic alloy possess high strength properties compare to the crystalline materials and it is possible only due to the modification of microstructure [41].

#### (ii) Addition of alloying elements for strengthening of alloys

The addition of alloying elements is one of the simplest and most efficient methods for enhancing the mechanical properties of Al alloys. The strengthening mechanisms can be explained by the impediment to dislocation motion produced by the precipitate formation or by substitutional or interstitial solid solutions of the alloying elements in the Al matrix. **Fig. 1.3 and 1.4** illustrate a schematic illustration of substitutional and interstitial solid solution strengthening, respectively. The Hume Rothery principles are a series of laws that govern the solubility of alloying components in order to generate a solid solution. The rules for forming a substitutional solid solution in the Al matrix for an alloying element are as follows:

i) The atomic radius difference between the solute and solvent atoms should be less than 15%.

ii) The crystal structure and electronegativity values of the solute and solvent should be identical.

iii) For a solute atom to dissolve entirely in a solvent, both of its valencies must be the same.



Fig. 1.3 Schematic of (a) substitutional solid solution (b) Dislocation stopped by substitutional atom

Whereas in interstitial solid solution, the alloying elements occupy the interstitial positions in the host element crystal structure. The following are the governing rules for the formation of interstitial solid solution:

i) The solute atoms must be smaller than solvent atoms in such a way that the difference in atomic radius should be  $\geq 15\%$ .

ii) The solute and solvent must have equal valency and electronegativities.

The relative size difference between the solute and solvent determines the amount of strength that the alloying element contributes. The crystalline lattice distorts more when there is a large size difference, as seen in **Fig. 1.5**. This additional distortion makes it even more difficult for dislocations to grow, improving strength.



**Fig. 1.4** (a) interstitial solid solution (b) Dislocation stopped by an interstitial atom



Fig 1.5 Effect of Solute size (a) same size (b) Big size solute (c) Small size solute

## **1.2.4 Status of properties enhancement in Al based** multicomponent alloys

In the present scenario, there is a huge demand of high-performance Al based alloys with stable microstructure with superior properties. Aluminium and its alloys having enormous industrial significance due to their outstanding properties. These properties can be obtained by altering the microstructure by adding the different alloying elements. Alloying elements, when added to Al alloys, can alter metallic and intermetallic phases, precipitation hardening, solid solution hardening, dispersion strengthening, grain refinement, suppression of grain growth, wear resistance, and other tribological properties. The selection of the alloying elements is based on their effects and suitability. The alloying elements can be major or minor elements. To enhance the mechanical properties of eutectic and near-eutectic Al-Si alloys, Yang et al. [18] reported the effects of various alloying elements, such as Cu, Ni, etc. The various intermetallics phases like Al<sub>2</sub>Cu, Al<sub>3</sub>Ni, Al<sub>3</sub>Ni<sub>2</sub>, Al<sub>3</sub>CuNi, Al<sub>7</sub>Cu<sub>4</sub>Ni etc forms by the addition of Cu and Ni in Al based alloys which contributes to the increase of excellent mechanical properties [42]. The addition of transition elements like Cu, Ni, Si is the most efficient and widely used technique to enhance the mechanical properties of Al based alloy at room temperature and at elevated temperature [43]. The SEM micrographs of the Al-Cu-Si alloy with the addition of Ni is shown in fig.1.6. It is clear from fig. 1.6 that with the addition of Ni, Al<sub>7</sub>Cu<sub>4</sub>Ni intermetallics phase formation is increasing and eutectic structure is also refined. The effect of Ni content on the

microstructure and mechanical properties of Al-Cu-Si alloy was investigated by Samuel et. al [11] reported a significant increase of the UTS and YS of the alloy after addition of 1.5 % Ni from 117 MPa to 272 MPa and 96 MPa to 267 MPa at 300°C respectively. This strength is very high compare to the conventional A319 Al alloy like tensile strength and yield strength is 199% and 214 % higher after addition of 1.5 % Ni as shown in **fig. 1.7**.



**Fig. 1.6** SEM micrographs of Al-Cu-Si alloy with the addition of Ni having (a) 0% (b) 0.7% (c) 1 % (d) 1.5% [43]

Pandey et al. [14] reported the effect of Cr on Al-Ni alloy with the change in microstructure or morphological transition of eutectic cell from rod to plate morphology having high strength at elevated temperature. The variation of yield strength with the addition of Cr is shown in **fig. 1.8**. All Cr containing Al-Ni alloys have higher strength compared to the binary Al-Ni alloy and the increment of the strength is almost 1.5 to 2 times. The YS values at room temperature, 200 °C and 250 °C are  $390 \pm 20$  MPa,  $275\pm15$  MPa and  $232\pm5$  MPa respectively which are very high compared to the conventional Al based alloy. The main reasons for strengthening are the refinement of grains and bimodal eutectic formation due to the addition of Cr. The SEM micrograph show the bimodal eutectic formation for 0.6 % Cr addition as shown in **fig. 1.9**.



**Fig. 1.7** Comparison of UTS, YS and %elongation of Al-Cu-Si eutectic alloy and conventional A319 alloy at elevated temperature [43]



**Fig. 1.8** Enhancement of YS with the addition of Cr element in Al-Ni alloy at (a) Room temperature (b) 200°C (c) 250°C (Insets show the stress-strain curve and enhancement of tensile strength) [14]



Fig. 1.9 SEM Micrograph in the BSE mode of suction-cast Al-4Ni-

0.6Cr alloy (higher magnification on right side) [14] Zeren et al. [29] reported the effect of Cu addition on the microstructure evolution and hardness of near eutectic Al-Si alloy. Due to precipitation hardening, the hardness improves as the Cu content increases. The hardness is found to increase from HB 55 to HB 118 when the Cu concentration is increased from 3% to 5%. Kaya et al. [44] also reported the effect of different alloying elements such as Cu, Co and Ni on the evolution of microstructure and mechanical properties of Al-Si-X alloy. It is observed that with the addition of different alloying elements, tensile strength and hardness of the Al-Si alloy increased from 65 MPa to 104 MPa and 60 MPa to 84.61 MPa respectively as shown in **fig. 1.10**. It is also observed that the addition of different alloying elements changed the microstructure of the Al-Si alloy to finer Si flakes and it is observed for Al-Si-Co alloy. It is also confirmed the best properties of Al-Si-Co alloy.





Yin et al. [45] has reported that by the addition of Sc and Zr in Al-Mg alloy, strength of the alloy increased by 150 MPa due to fine grain and precipitation strengthening. Average grain size is refined from 370  $\mu$ m to 72  $\mu$ m and after adding both elements simultaneously the grain size is reduced up to 42  $\mu$ m. After adding copper to the al alloys, it increases the strength but reduce the ductility. By adding Mn to al alloy, it will increase the strength and no effect on ductility. Si reduces the melting point and increase the fluidity of Al alloy. Effect of other elements like Zn, Fe, Cr, Ti, Ni, Li, Pb, Bi etc on al based alloys also reported. Therefore, according to the suitability and desired properties, we can select and add different alloying elements to alter the properties of Al based alloy. Joseph et al. [46] also reported the effect of different alloying elements on the corrosion behaviour, wear behaviour, different processing and grain boundaries of Al based alloys. Joseph has reported the effect of Cu, Mg, Mn, Fe, Mo, Si, Zn etc. on the mechanical

properties of Al rich alloys. So, we can say that the alloying elements change the microstructure during the solidification process by introducing a new element into the exist alloy. As a result, the solidification process is crucial to understanding phase equilibria and the development of the microstructure in any alloy.

#### 1.3 Solidification behaviour analysis by Numerical approach

Metal casting is one of the required steps to develop any alloy. It is a direct method of manufacturing to obtain the product in a desired shape and size. In the foundry sector, casting rejections are a serious problem. If the casting design can be changed prior to moulding on the basis of defect prediction, significant material, energy, and time savings can be achieved. Numerical solidification simulation is an effective tool for producing high-quality castings while reducing product cost and scrap [47].

Casting processes have been mathematically modelled since the mid-1960s. With the continued success and popularity of computers, particularly after the 1980s, an increasing number of researchers have become involved in casting simulation research, development, and application [48]. The way the casting industry operates has been transformed by mathematical modelling. simulation allows for advanced analysis and optimization as well as proactive intervention. By reducing the development time, removing product defects, and reducing expenses, simulation can improve product quality as well as production efficiency. Many casting simulation models have been developed and some of them are available for purchase. Casting process optimization may be possible by simulation of casting solidification [47]. To fully exploit this potential, all heat transmission phenomena inside the casting system must be precisely represented. The metal/mould interface is a significant component of heat transfer in the system. Heat transfer at the cast metal/mould contact is difficult to monitor and quantify due to a variety of complicating factors. Interfacial heat transfer is influenced by the casting alloy, the mould material and coating, the casting process variables, and the casting geometry. Many scientific and engineering applications involve solid/liquid phase change, such as crystal growth [49], casting processes etc. Experiments that are carefully constructed and thoroughly characterised, as well as advanced numerical modelling approaches, are required to investigate the heat transfer processes, as well as the solidification mechanisms, that are involved in these applications [50]. Aluminium, copper, iron, and steel foundries employ casting solidification simulation software to simulate processes such as investment and gravity die casting [51]. Swaminathan et al. [52] has reported an enthalpy method for solidification simulation process by introducing the simulation numerical model for solidification of steel ingot, cast steel billets, Al-4.5Cu alloy, Pb-10Sn alloy etc with good agreement and implemented this method to control volume and finite element method. Bhatt et al. [53] has reported the solidification simulation to optimize the feeding system and to find out the correct location of riser because feeding system is the very important part to produce the good quality castings. Temperature distribution during the casting process with the different location of risers is shown in fig. 1.11. The conclusion of the work is that casting Simulation is a great tool for predicting the evolution of a process without having to physically do it. On a simulation software programme, a large number of experiments may be carried out fast, and the best possible result can be acquired, increasing the foundry's profit margin. The methods engineer's confidence in the functionality of the feeding system design is also increased through simulation. M.Choudhari et al. [54] reported the modelling and simulation of aluminium during the sand-casting process for 3600 secs and identified the last hotspot region and isotherms that improve the casting quality. Temperature contours at the different time instant during the solidification and the computation domain with meshed area is shown in fig. 1.12. The use of software to determine the best location for the riser by identify last hotspot region has helped to reduce solidification- related faults, resulting in a defect-free casting (no internal cavity)



**Fig. 1.11** (a) Solid model for casting (b to d) Simulation results with distribution of temperature during different trials (e) Temperature Scale [53]





Pariona et. al. [55] reported the solidification simulation of pure iron in sand and mullite mould for 1.5 hours using ANSYS Fluent software with cooling and heating curves and compared the physical properties of sand

and mullite system. Temperature distribution profiles in the both cast metal zone and both mould after the completing of solidification are shown in **fig. 1.13**. **Fig. 1.13** show the temperature variation from 555 K to 1321 K in sand mould and 803 K to 886 K in mullite mould. The large temperature variation in sand mould confirms the physical properties of sand mould which is different from mullite mould.



Fig.1.13 Temperature distribution profiles after 1.5 hr of simulation in(a) Sand mould (b) Mullite mould (c) Cast metal in sand mould (d)Cast metal in mullite mould [55]

During the solidification, the variation of temperature with the time (cooling curves) is the important parameter to visualize the phase transformation and therefore, Pariona has reported the cooling curves in cast metal zone at some selected points (1 to 5) and heating and cooling curves in the mould zone at the selected points (6 to 14) during the solidification process as shown in **fig. 1.14**. The abovementioned points are selected in the computational domain. In **fig. 1.14 (c)**, phase transformation temperatures at point 3 & 4 are 1816 K (from liquid iron to  $\delta$ -iron) and 1671 K (from  $\delta$ -iron to  $\gamma$ -iron) respectively. This transformation also validates the simulation results. On the base of these results, the author has reported the cooling behaviour, grain size and mechanical properties of the metal during the solidification in both moulds.



**Fig. 1.14** (a, b) Selected points and path in cast metal with sand and mullite mould respectively (c, d) Cooling curves (e, f) Heating and cooling curves in sand and mullite mould respectively [55]

Ojha et. al [56] investigated the solidification simulation of AlSi10Mg alloys using a direct metal laser sintering (DMLS) process using ANSYS platform to understand the solidification process. For this purpose, a 3D simulation model was developed by using FVM method in ANSYS software for DMLS process to investigate the evolution of temperature and solidification phenomena. Computation domain, temperature profiles, velocity vector profiles and solidification profiles during the DMLS process is shown in **fig. 1.15**. **Fig. 1.15** shows the complete understanding of the heat transfer and solidification phenomena. Kadhim Eqal et al. [57] has reported a prediction of the solidification profiles during the solidification profiles during the solidification profiles are shown in **fig. 1.16** for all three alloys. The difference in the liquid mass fraction with the decreasing temperature of studied three alloys is shown in **fig. 1.17** (a) which shows that freezing start point is greater for higher

content of aluminium content. **Fig. 1.17** (**b**) shows the variation of mass fraction with time and therefore it reflects the type of solidification like slow solidification at initial stage and rapid solidification after 10 sec. **Fig. 1.17** (**c**) shows the cooling curves in the mushy zone region for all three alloys.



**Fig. 1.15** Solidification simulation model (a) Computational domain for simulation (b) Temperature profiles (c) Velocity vector profiles (d) Solidification profiles of AlSi10Mg powder bed in DMLS process [56]

Zheng et al. [58] also reported the 3D numerical model of splat formation using ANSYS Fluent 14 software and phase profile and temperature contours at different spreading times the droplet are shown in **fig. 1.18 & 1.19** respectively. The simulated and experimental results show good agreement.



**Fig.1.16** Contours of the liquid fraction during solidification of (A) ZA 8 (B) ZA 12 (C) ZA 27 alloys [57]



Fig.1.17 (a) Variation of liquid mass fraction with temperature after 24 sec (b) Variation in the solid mass fraction with time (c) Cooling curve during solidification [57]





Sahoo et. al. [59] demonstrated the solidification simulation of Al-33Cu alloy during the twin-roll casting process using ANSYS Fluent software and compare the microhardness results with the cooling rate. Venkatesan et al. [47] reported the solidification simulation of Al-6wt%Si alloy in sand mould and steel mould using a developed program and validated with ANSYS software simulation results and stated that

simulation is helpful to minimize the casting defects during the experimental work.



Fig.1.19 Temperature contours inside the droplet and substrate at different flattening times [58]

Hussainy et. al. [60] investigated the solidification simulation for A356 aluminium alloy in silica sand mould with and without interface resistance and validated the results with experimental work within 15% error and found that the solidification simulation is helpful to optimize the casting process. Teng ma et. al. [61] reported the solidification simulation of Al-10Mg alloy using a twin-roll casting process which describes accurately the actual solidification process using the mathematical modelling approach. Trindade et al. [62] has reported the modelling of solidification of continuous casting with mold electromagnetic stirring to evaluate heat extraction in the mold region in a better way using ANSYS Fluent software.

# **1.4 Development of high strength eutectic high entropy alloys for high-temperature applications**

#### **1.4.1 Introduction**

### (i) High Entropy Alloys

From the thousands of years, the development of alloy system is mainly based on one principal element like Al based, Cu based, Ni based alloys etc with the addition of minor alloying elements to enhance the properties [5]. After that from last 5 decades, intermetallics compounds have attracted material community and binary and ternary alloys were derived like Al-Fe, Al-Ni, Ti-Al, Al-Si, Al-Si-Cu, Al-Fe-Ni etc but the design concept is based on the one principal element. Recently, a new class of alloys which are multi-Principal element alloys or HEAs appeared as a new research frontier in the research community after the first proposed by yeh et. al. The development of HEA has opened up new possibilities for developing novel materials with excellent qualities such as high fatigue and wear resistance, high corrosion resistance, high hardness, high hot strength, good combination of strength and ductility and so on [63–66].

#### (ii) Eutectic high entropy alloys (EHEAs)

In recent years, the eutectic alloys have been attracted more attention by the materials research community due to easy processing and excellent mechanical properties. It is reported that eutectic alloys are designed and developed in the binary alloys as well as multicomponent alloys such as ternary alloys, quaternary alloys [12], quinary alloys etc. with the help of phase diagrams and hence considered as potential advanced material due to their excellent properties as compared to single-phase alloys [33]. Depending on the cooling rate, several different forms of microstructures can be seen in the eutectic alloy [34, 35]. Mechanical properties of the eutectic alloys having lamellar microstructure and the mixture of soft solid solution phase and hard intermetallic phase exhibit excellent mechanical properties [36-38]. Albeit several eutectic alloys have been studied for various applications but only a few alloys have been identified for commercial applications [67]. Recently, a new class of alloys which are popularly known as multi-principal multicomponent alloys or HEAs appeared as a new research frontier in the research community after the first proposed by Yeh et. al. [5]. The development of HEAs opened up new possibilities for developing novel materials with excellent properties such as high fatigue and wear resistance, high corrosion resistance, high hardness, high hot strength, and so on[63-65, 68].

HEAs are defined as equiatomic or nearly equiatomic multicomponent alloys, consisting of at least 5 principal elements, which are different from the conventional alloys having one or two principal elements. After the discovery of HEAs in 2004, the design and development of single-phase HEAs have been extensively researched by varying the concentration of each element, ranging from 5 atomic % to 35 atomic %, due to the formation simple microstructure with solid solution phase(s) such as FCC and/or BCC solid solution phase(s) which are attributed to the four core effects such as high configurational entropy, lattice distortion effect, sluggish diffusion and cocktail effect [69]. These core effects act as a barrier for the formation of the complex phases in HEAs and exhibits outstanding properties at high temperatures [70, 71], High corrosion resistance [72], high wear resistance [73] and high hardness [74, 75]. Therefore, HEAs are considered as potential engineering materials for structural applications for high temperatures. It is noteworthy to mention that the single-phase FCC HEAs show better ductility but not enough strength [76]; whereas single-phase BCC HEAs show better strength but not enough ductility [77]. It is also observed that there are some other difficulties during the processing of HEAs such as poor castability and chemical inhomogeneity which also limits the uses of HEAs for industrial applications [78]. To circumvent the abovesaid problems, the new class of HEAs have been designed and developed, which is known as EHEAs, consisting a mixture of solid solution phase(s) and intermetallic. It is reported that EHEAs show good castability due to single melting temperature, improved mechanical properties, high temperature creep resistance, high rupture strength, controllable microstructure etc [79, 80]. It is interesting to note that the EHEAs, having a combination of the primary dendritic phase and eutectics show better combination of strength and ductility as compared to the fully eutectic microstructure in EHEAs [81]. Numerous studies have investigated the stability of the EHEAs, and findings indicate that even after high-temperature heat treatment processing, the EHEAs have good mechanical properties [66].

As a result, it is anticipated that the field of EHEAs will continue to be active for researchers in the near future and bring hope for the development of materials with superior properties. Hence, EHEAs are considered as promising materials for high temperature structural applications.

#### 1.4.2 Design Methodology for multicomponent EHEAs

It is reported that EHEAs are considered as an important class of materials for structural applications due to outstanding mixture of mechanical properties and ease of processing. Interlamellar spacing ( $\lambda$ ) is considered as the characteristic length scale in eutectic microstructure. According to the Hall patch equation [82], the YS of the eutectic alloy depends on the interlamellar spacing ( $\lambda$ ). The Hall patch equation expression is defined by the following equation,  $\sigma_{ye} = \sigma_{oe} + K_e \lambda^{(-1/2)}$ ; where  $\sigma_{ve}$  is the YS, K<sub>e</sub> is the slope which is named as Hall-Patch slope and  $\lambda$  is the interlamellar spacing. It is clear from the above equation that the strength of the eutectic alloy can be increased by reduction of the interlamellar spacing ( $\lambda$ ). It is also possible to lower the interlamellar spacing to the nanometre (nm) range by adopting suitable processing parameters [27]. To achieve the balance combination of mechanical properties, the EHEA, having primary dendrite microstructure and eutectics should be developed. To develop ultrafine/nano eutectic microstructure in EHEAs, the semi-quantitative analysis, highlighted in Jackson-Hunt (JH) model is given in the followings.

According to the Jackson-Hunt (JH) model [83–85], a relationship between  $\lambda$  and solidification front velocity (V) is expressed by the given equation:

$$V^{1/2}\lambda = A \tag{1.1}$$

;where A is defined as  $A = \frac{K_2}{K_1}$  (1.2)

; where  $K_1$  and  $K_2$  can be expressed by the relationship

$$K_1 = \frac{m_V c_{\alpha\beta} P}{D f_\alpha f_\beta} \tag{1.3}$$

$$K_2 = 2m_V \sum_i \frac{\Gamma_i \sin\theta_i}{m_i^V f_i}; (i = \alpha, \beta)$$
(1.4)

;where  $m_V$  is the liquidus slope which depends on velocity,  $C_{\alpha\beta}$  is the eutectic compositional range, D is the diffusion coefficient,  $\theta_i$  is the contact angle between the liquid and solid phase at the triple point,  $\Gamma_i$  is the capillary constant and  $f_i$  is the volume fraction of the solid phase. The velocity-dependent liquidus slope  $m_V$  can be calculated with the help of liquidus slope of individual phase and is expressed by the following expression

$$\frac{1}{|m_V|} = \frac{1}{|m_{\alpha}|} + \frac{1}{|m_{\beta}|} \tag{1.5}$$

;where  $m_{\alpha}$  is the liquidus slope of  $\alpha$  phase and  $m_{\beta}$  is the liquidus slope of the  $\beta$  phase.

$$P = \sum_{i=1}^{\infty} \left(\frac{1}{n\pi}\right)^2 [\sin(n\pi f)]^2 \frac{P_n}{\sqrt{1 + P_n^2 - 1 + 2K(V)}}$$
(1.6)

; where 
$$P_n = \left(\frac{2n\pi}{P_e}\right)$$
 and  $P_e = \frac{V\lambda}{2D}$  (1.7)

It is observed from the above equations that interlamellar spacing ( $\lambda$ ) depends on the following parameters: (i) D, (ii)  $C_{\alpha\beta}$ , (iii) m<sub>a</sub> & m<sub>\beta</sub> and (iv)  $\theta_i$ . The higher values of liquidus slope and smaller value of diffusion coefficient lead to smaller interlamellar spacing ( $\lambda$ ) for a given solidification front velocity. The sluggish diffusion effect in the EHEAs is in the favour of achieving low value of the diffusion coefficient (D) and therefore favouring formation of the ultrafine or nanoscale interlamellar spacing in EHEAs. This analysis gives an idea to obtain ultrafine/nanoscale eutectic by judicious selection of alloying elements and the composition of EHEAs.

#### 1.4.3 Mechanical Properties enhancement mechanism of HEAs

Conventional alloys enhance the properties of the principal element by adding a number of alloying elements, but because there are only few elements in the periodic table, there are only a few alloys that can be made. Therefore, to eliminate this limitation, multicomponent alloys or HEAs were developed by cantor et al. [86] and yeh et al. [5] in 2004. The invention of HEAs is a breakthrough in traditional physical metallurgy for alloy design, and it opens up a new sector for the discovery of novel alloys with specific qualities. HEAs have unique qualities that are dependent on microstructure development, and are thus used as a structural engineering material [87]. However, researchers have challenges in obtaining improved mechanical qualities such as strength and ductility, which must be overcome. According to the literature [88, 89] single-phase HEAs have been shown to have a problem balancing ductility and tensile strength. Single-phase FCC HEAs due to the FCC crystal structure, but they do not provide enough strength to safeguard against fracture in service [90]. Whereas BCC crystal structure based single-phase HEAs shows better strength with brittleness [77].

As a result, researchers are focusing their efforts on composite HEAs to address the mechanical characteristics issue. To tackle this challenge, the researchers created HEAs with a composite microstructure that included both BCC and FCC phases. As a result, a thorough understanding of HEA phase equilibria and solidification behaviour is required [91]. In addition, there are several processing challenges with HEAs, such as poor castability and chemical inhomogeneity, which limit their use in engineering applications [92]. Finally, the researchers devised EHEAs, which have a microstructure made up of a mix of FCC and BCC phases. EHEAs have been found to be ductile and strong . EHEAs are also said to have advantages including a low energy phase boundary, strong rupture strength, superior high temperature creep resistance, adjustable microstructure, stable flaws structures, and near equilibrium microstructures [93]. EHEAs were used to tackle the above poor cast-ability problem, and as a result, the EHEAs have enhanced mechanical qualities in terms of strength and ductility.

#### 1.4.4 Status on the development of HEAs

The HEAs are different from the conventional alloys as 4 to 5 principal elements are used instead of one or two principal elements. After the development of HEA in 2004, they focused to produce the single-phase alloy systems by varying the element concentration which varies from 5 atomic % to 35 atomic %. The HEA shows the simple microstructure which are attributed to the effect of principal alloying elements in the equiatomic ratio or nearly equiatomic ratio. Some basic effects [88] including as high mixing entropy, lattice distortion effect, and sluggish diffusion, are responsible for HEAs' simple microstructure [69]. These core effects act as a barrier for the development of the complex phases and slow down the kinetics of the phase formation process. HEAs have a lot of superior properties such as admirable ductility at high temperatures [70, 71], High corrosion resistance [72], high wear resistance [73] and high hardness [74, 75] at high temperatures. Due to the unique properties of the HEAs at elevated temperatures, these alloys are considered engineering materials for structural applications for high temperatures. Even after these unique properties, many researchers are facing some problems to obtain the mechanical properties in the better combination. It is noteworthy to mention that the single-phase FCC HEAs show better ductility but not enough strength [76] whereas single-phase BCC HEAs show better strength but not enough ductility [77] for structural applications. With these problems, there are some other difficulties during the processing of HEAs such as poor castability and chemical inhomogeneity which also limit the uses of HEAs for industrial applications [78]. To solve the abovesaid problems, the research community is trying to develop the EHEAs which are consisting a mixture of FCC and BCC phases. It is reported that EHEAs show good strength as well as ductility. The other advantages of the EHEAs are high temperature creep resistance, high rupture strength, controllable microstructure etc[80]. Therefore, EHEAs are promising materials in terms of strength and ductility and other properties for the use of engineering applications. The strength and good castability of EHEAs made them potential candidates for high-temperature applications. The EHEAs which are having a combination of the primary phase and eutectic phase gives a better combination of ductility and strength compared to the fully eutectic HEAs [81].

#### 1.4.5 Design strategy for multicomponent EHEAs

Although the design of the EHEAs is challenging for the research community, the researchers are using different methods to design the EHEAs such as the simple mixture method [94], CALPHAD method[95], use of thermo-physical properties [96], mixing enthalpy method [97], machine learning approach etc [98]. The CALPHAD method is considered as effective method design the EHEAs. To predict the evolution of phases, phase(s) stability and also to design novel EHEAs for high-temperature applications, three approaches are explained below:

#### (i) Phenomenological criteria using thermo-physical parameters

To achieve superior mechanical properties, the phase selection and processing routes are the most critical parameters for the design of EHEAs with the ultrafine/ nanoscale microstructural features. The phase stabilization in the EHEAs depends on many thermo-physical parameters. As a result, the parameters for designing EHEAs with phase stability at non-equilibrium conditions must be identified [99, 100].

#### (a) Enthalpy of mixing $(\Delta H_{mix})$

The change in Gibbs free energy after the mixing of elements in HEAs is expressed by  $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$  [40]. Intermetallic or Laves phase instead of single solid solution phase can be evolved with the highly negative value of enthalpy of mixing. As a result, one of the most crucial variables to ascertain the phase development in EHEAs is the enthalpy of mixing and is defined as [101]

$$\Delta \mathcal{H}_{\mathrm{mix}} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} C_i C_j \tag{1.8}$$

; where  $C_i$  and  $C_j$  are defined as the molar fraction of the i<sup>th</sup> and j<sup>th</sup> element of alloy respectively and n is the number of elements in the alloy system.  $\Omega_{ij}$  is defined as  $\Omega_{ij} = 4 \Delta H_{mix}^{ij}$ , where  $\Delta H_{mix}$  is the mixing enthalpy of a binary alloy having i<sup>th</sup> and j<sup>th</sup> elements.

#### (b) Atomic size difference $(\delta_e)$

The atomic size of alloying elements plays also significant role in predicting the phase formation in EHEAs. The atomic size difference is defined as [101].

$$\delta_{\rm e} = \sqrt{\sum_{i=1}^{n} C_i (1 - \frac{r_i}{\bar{r}})^2}$$
(1.9)

; where  $C_i$  is the concentration or molar fraction of the i<sup>th</sup> element,  $r_i$  is the atomic radius of i<sup>th</sup> element and  $\bar{r}$  is the mean atomic radius of an alloy and it is expressed by  $\bar{r} = \sum_{i=1}^{n} C_i r_i$ 

The relationship between  $\Delta H_{mix}$  and  $\delta_e$  is explained by Chanda et al. [99] Based on a survey for many EHEAs and the relation is shown in **Fig. 1.20a**. The relationship shows the highly negative values of mixing of enthalpy are indication of forming EHEAs.



**Fig.1.20** (a) Relationship between  $\Delta H_{mix}$  and  $\delta_e$  (b) Relationship between VEC and  $\delta_e$ , for EHEAs, single-phase FCC and BCC phase HEAs [99]

#### (c) Valence electron concentration (VEC)

The thermodynamic parameter, VEC determines the structure of the phases which are formed during the processing of EHEAs and is given by the expression as given below:

$$\text{VEC} = \sum_{i=1}^{n} C_i (VEC)_i \tag{1.10}$$

; where  $(VEC)_i$  is the valence electron concentration of the i<sup>th</sup> element.

If the value of VEC

(i) VEC  $\geq$  8 (Possibility of formation of FCC solid solution phase only)

(ii) 6.87 ≤ VEC < 8 (Possibility of formation of mixture of phases i.e.,</li>FCC, BCC and Intermetallic)

(iii) VEC < 6.87 (Possibility of formation of BCC phase only)

The relationship between VEC and  $\delta_e$  is explained by Chanda et al. [99] based on a survey for many EHEAs and is shown in **Fig. 1.20b**.

#### (d) Entropy of mixing $(\Delta S_{mix})$

The mixing entropy  $(\Delta S_{mix})$  helps in the formation of solid solution phase(s) in the HEAs and is expressed by

$$\Delta S_{\min} = -R \sum_{i=1}^{n} C_i ln C_i$$
(1.11)

To reveal the combined effect of  $\Delta H_{mix}$  and  $\Delta S_{mix}$  on the formation of phase evolution and stability, a new parameter is introduced and is given by

$$\Omega = \frac{T_m \Delta S_{mix}}{\Delta H_{mix}} \tag{1.12}$$

; where R is the universal gas constant and  $T_m$  is the average melting temperature and it is defined by

$$T_m = \sum_{i=1}^n C_i T_{m_i} \tag{1.13}$$

For solid solution phase formation, the value of  $\Omega$  must be positive, and  $\Omega = 1$  is taken as a critical value to form the solid solution. If  $\Omega > 1$ , the term (T<sub>m</sub>)  $\Delta S_{mix}$  will exceed that of  $\Delta$ Hmix for solid-solution phase formation. If  $\Omega \leq 1$ ,  $\Delta$ Hmix is the predominant factor, which leads to the formation of intermetallic compounds and segregations. Thus, the value of  $\Omega$  is taken into consideration to estimate the solid solution phase formation in HEAs.

#### (e) $\Lambda$ - Parameter

The parameter  $\Lambda$  is generally used to study the understanding of the collective behaviour of  $\Delta S_{mix}$  and  $\delta$ .  $\Delta S_{mix}$  and  $\delta$  play an essential role in predicting the formation of solid solution phase(s) in the HEAs. The parameter  $\Lambda$  is expressed as [102].

$$\Lambda = \frac{\Delta S_{mix}}{\delta^2} \tag{1.14}$$

If the value of  $\Lambda$  – Parameter is greater than equal 2.3403, it leads to the formation of a single-phase formation in HEAs, and if the  $\Lambda$  – Parameter value lies between 0.3165 to 0.5425, the mixture of both solid solution phase and Laves phase formation is possible in HEAs. If  $\Lambda$  – Parameter value is less than equal to 0.2567, there is possibility of formation of the solid solution phase, Laves phase, and intermetallic.

#### (f) Allen electronegativity $(\Delta \chi_A)$

The electronegativity difference is a Hume-Rothery factor that is generally used to determine intermetallic formation in the complex alloy system which plays an vital role in predicting the formation of intermetallic in the HEA and it is expressed by

$$\Delta \chi_{A} = \sqrt{\sum_{i=1}^{n} (1 - \chi_{i}^{A} - \chi_{a})^{2}}$$
(1.15)

; where  $\chi_i^A$  is the Allen electronegativity of i<sup>th</sup> element and  $\chi_a$  is the average Allen electronegativity which is calculated by

$$\chi_a = \sum_{i=1}^n C_i \chi_i^A \tag{1.16}$$

It is clear from **Fig. 1.21** that to develop an EHEA,  $\Delta \chi_A$  should be greater than 5.5% and atomic size difference should be greater than 3% and the new parameter  $\Omega$  should be in the range of 0.85 to 2.

The atomic size difference ( $\delta_e$ ) should be high for EHEAs because destabilization of the simple phases will occur due to the increase of lattice strain. Therefore, alloy concentration is the main control factor for the

evaluation of eutectic phases, which affects both the thermodynamic parameters such as  $\Delta H_{mix}$  and  $\delta_e$ .



**Fig.1.21** (a)  $\Omega$  vs.  $\delta$  showing the evolution of different phases with the addition of Nb in CoCrFeNiNb<sub>X</sub> (b) Electronegativity vs.  $\delta$  to predict phases evolution in CoCrFeNiNb<sub>X</sub> and other reported EHEAs [100]

The addition of Nb/Ta to an FCC single-phase CoCrFeNi HEA has been reported to destabilise the single-phase into a two-phase eutectic microstructure, leading to the formation of FCC solid solution phase and Laves phase [99]. Since it is known that the atomic radius of Nb/Ta is higher than other elements present in the alloy system and the Nb/Ta have a higher negative value of  $\Delta H_{mix}$  compared to the other elements present in the alloy system. It is to be noted that VEC is also an essential parameter to determine the stability of phases in EHEAs. On the basis of **Fig.1.20 and 1.21**, it is reported that the range for different thermodynamic parameters for design of EHEAs are given as;  $-18 \leq \Delta H_{mix} \leq -6$ , 6 < VEC< 8.5,  $\delta_e > 3\%$ ,  $\Delta \chi_A > 5.5\%$  [99].

Lu et al. [97] have designed and developed four different types of EHEAs using the mixing enthalpy method. After searching the mixing enthalpy for atomic pairs using different refractory elements, Lu et. al. found that Zr, Nb, Hf and Ta possess highly negative mixing enthalpy with Ni. Therefore, new EHEAs can be designed and developed by replacing Al in AlCoCrFeNi<sub>2.1</sub> with Zr, Nb, Hf and Ta. The SEM micrographs of the newly developed EHEAs, consisting of two phases are shown in **Fig. 1.22**. Lu et al have concluded that the mixing enthalpy method has high efficiency and accuracy to design the EHEAs.



**Fig.1.22** SEM micrographs of four EHEAs designed by mixing enthalpy method (a) Zr<sub>0.6</sub>CoCrFeNi<sub>2</sub> (b) Nb<sub>0.74</sub>CoCrFeNi<sub>2</sub> (c) Hf<sub>0.55</sub>CoCrFeNi<sub>2</sub> (d) Ta<sub>0.65</sub>CoCrFeNi<sub>2</sub> [97]

It is reported that different types of EHEAs have been developed using thermo-physical parameters, which are shown in the **Table 1.1** 

**Table.1.1** The calculated value of thermophysical parameters such as  $\Delta S_{mix}, \Delta H_{mix}, \delta_e$ , VEC and the Microstructure details having eutectic phases in EHEAs

Alloys	Eutectic	$\Delta S_{mix}$	$\Delta H_{mix}$	$\delta_{e}$	VEC	Referen
	Phases					ces
CoCrFeNiNb <sub>0.45</sub>	FCC+	13.08	-10.12	4.9	7.92	[99]
	Laves					
CoCrFeNiNb <sub>0.65</sub>	FCC+	13.28	-12.15	5.56	7.80	[99]
	Laves					
CoCrFeNiTa <sub>0.2</sub>	FCC+	12.57	-6.80	3.59	8.1	[99]
	Laves					
CoCrFeNiTa <sub>0.5</sub>	FCC+	13.15	-10.37	5.09	7.89	[99]
	Laves					
Co <sub>2</sub> Mo <sub>0.6</sub> Ni <sub>2</sub> VW <sub>0.6</sub>	$FCC + \mu$	12.27	-8.72	4.69	8.10	[103]
Co <sub>2</sub> MoNi <sub>2</sub> VW	$FCC + \mu$	12.89	-7.92	5.04	7.86	
AlCrFeNi	<i>BCC</i> + <i>B</i> 2	11.53	-13.25	5.75	6.75	[104]
Al <sub>1.3</sub> CrFeNi	<i>BCC</i> + <i>B</i> 2	11.47	-14.26	6.04	6.49	

AlCoCrFeNb <sub>0.5</sub> Ni	BCC+	14.70	-16.53	6.32	7	[105]
	Laves					
AlCoCrFeNb <sub>0.75</sub> Ni	BCC+	14.85	-18.03	6.59	6.91	
	Laves					
Al <sub>2.1</sub> CrCuFeNi <sub>2</sub>	FCC+	12.85	-9.89	6.03	7.23	[106]
	BCC					
CoFeNiVMo <sub>0.6</sub>	FCC+	13.24	-9.53	4.2	7.74	[107]
	CoMo <sub>2</sub> Ni					
CoFeNiVMo	FCC+	13.38	-8.96	4.54	7.6	
	Co <sub>2</sub> Mo <sub>3</sub>					
CoFeNi <sub>1.4</sub> VMo	FCC+	13.30	-9.16	4.53	7.78	
	$Co_2Mo_3$					
CoFeNi <sub>1.8</sub> VMo	FCC+	13.1	-9.23	4.5	7.93	
	$Co_2Mo_3$					

# (ii) CALPHAD approach to design higher order multicomponent EHEAs

Thermodynamic modelling is utilised to optimise the alloy parameters and gives the full potential to forecast development of desired phases in EHEAs by using CALPHAD approach. First of all, single-phase HEAs are developed by thermodynamic simulation technique. Secondly, EHEA can be designed with the addition of alloying elements in the single-phase HEA.

### (a) Design and development of seven components EHEA

The above-mentioned strategy has been well documented in the open literatures, such as the development of a seven-component EHEA by incorporating Nb into a six-component single-phase HEA [108]. The alloying element Nb is selected because the Nb element forms a eutectic system with Co, Ni, Fe and Cr and the eutectic range is selected from Nb 8 at% to 10 at% with the help of CALPHAD analysis as shown in **Fig. 1.23a**. The Scheil's solidification pathways for Nb<sub>8.66</sub>, Nb<sub>9.8</sub> is shown in **Fig. 1.23b** which confirm the evolution of FCC phase and C14 Laves phases during the solidification. The SEM images of the as-cast samples

are shown in **Fig. 1.23c** which showing the formation of eutectic microstructure in developed seven component HEAs. The hypereutectic and hypoeutectic microstructures are shown in **Fig. 1.23d & 1.23e**.



Fig.1.23 ThermoCalc and SEM results (a) Pseudo binary phase diagram, scheil's solidification curve for (b) Nb<sub>8.66</sub> (c) Nb<sub>9.8</sub>, SEM micrographs for (d) Nb<sub>8.66</sub> (e) Nb<sub>9.8</sub> [108]

#### (b) Design and development of eight components EHEA

The higher order eight components multicomponent EHEA was also reported using thermodynamic simulation technique [109]. First of all, the amount of phase vs. temperature and Scheil's solidification curve for seven components single-phase HEA Fe<sub>32.5</sub>Co<sub>10</sub>Ni<sub>25</sub>Cr<sub>15</sub>Mn<sub>5</sub>V<sub>10</sub>Al<sub>2.5</sub> are obtained with the help of thermodynamic simulation and then visualize the effect of Nb to produce the EHEAs. Because the mixing enthalpy of Nb is higher than that of Co, Cr, Fe, Ni, and hence EHEAs are developed by systematic addition of Nb. As a result, by including specific elements in the single-phase HEA, it is possible to produce an EHEA with a dualphase mixture structure. The exceptional strength and high oxidation properties of the Laves phase at high temperatures have been noted by numerous researchers as it's acting as a strengthening agent for engineered
materials [110]. Therefore, a novel multicomponent EHEAs for high temperature applications are designed by incorporating Nb alloying element in the single-phase HEA, leading to the formation of the dual-phase microstructure. SEM micrographs of the investigated EHEAs show the formation of eutectic microstructure with the addition of Nb element in the single-phase HEA (as shown in **Fig. 1.24a to 1.24c**). XRD analysis of seven component EHEAs is also shown in **Fig. 1.24d** which also confirms the formation of FCC solid solution phase and Laves phase.



Fig. 1.24 SEM Micrographs for8 components EHEA with (a) 5 at% Nb (b) 7.5 at% Nb (c) 12.5 at% Nb, XRD plot for (d) 8 components EHEA with the addition of Nb [109]

# (c) Machine learning approach to predict the phase formation in EHEAs

Machine Learning (ML) is widely used in various applications in the field of material science [98]. Islam et al. [111] has successfully predicted the phase formation in multicomponent alloys by using ANN approach with predictive accuracy of more than 90%. Wu et. al. [112] have used the combined approaches of CALPHAD, ML and experimental methods to predict and develop of EHEAs by using AlCoCrFeNi system. Krishna et. al.[98] have reported the phase prediction of EHEA by using 6 different algorithms such as Logistic Regression (LR), Random Forest (RF), Support Vector Machine (SVM) classifier, Gradient Boosting (GB), Decision Tree (DT) and Artificial Neural Network (ANN). The supervised learning approach [113, 114] is used for training the different algorithms by using the labelled data. For each algorithm, the optimum parameters were established using the "gridsearchcv" routine (where cv stand for cross validation) with the help of scikit learn library from the considered parameter space. This prediction was made using thermophysical parameters. It is important to consider all parameters for the statistical analysis because a single parameter is not sufficient to identify the phases in ML algorithm. A confusion matrix is also used to evaluate the performance of various algorithms with the help of normalized values of the actual and predicted phases. The confusion matrixes and prediction accuracy of different phases for different algorithms are shown in Fig. 1.25. It is clear from the Fig. 1.25, that the best prediction accuracy of both solid solution phase (SS) and intermetallics (IM) phase (i.e., SS + IM) is 78% using SVM algorithm. After training, all of the algorithms were utilised to predict the evolution of phases in EHEAs. The predictive capability of different algorithms is shown in Table 1.2 for HEAs.



**Fig. 1.25** Confusion matrixes of different algorithms (a) LR (b) DT (c) RF (d) GB classifier (e) SVM (f) ANN [98]

**Table.1.2** Prediction of different alloys using different algorithms,ThermoCalc data and Experimental data (The red and green colour showthe wrong and right prediction respectively) [98]

Composition	LR	SVM	GB	DT	RF	ANN	Thermo	Experime
							Calc	ntal
FeCoNi-10Nb							SS+IM	SS+IM
[98]								
CoCrNi-10Nb							SS+IM	SS+IM
[98]								
FeCoCrNi-10Nt							SS+IM	SS+IM
[113]								

#### 1.4.6 Microstructure and mechanical properties of EHEAs

In the following section, the microstructure development and mechanical properties of different types EHEAs are highlighted.

## (i) Microstructure and mechanical properties of (FCC+ Intermetallic) EHEAs

Dong et al. [115] prepared the AlCrFeMo<sub>0.2</sub>Ni HEA via vacuum induction melting, and the microstructure consists of lamellar and rod-type eutectics having FeCr-rich solid solution phase and AlNi-rich intermetallic and the effect on mechanical properties with electromagnetic field intensity is observed. It is found that compressive fracture strength and fracture strain first increase and then decrease, while hardness increases with increasing the electromagnetic field intensity. The highest fracture strength of 2282.3 MPa, yield strength of 1160.5 MPa, and fracture strain of 0.29 are observed at 15 mT electromagnetic field.

Jiang et al. [103] reported  $Co_2Mo_{0.8}Ni_2VW_{0.8}$  fully EHEA having FCC CoWMo-rich solid solution phase and  $Co_7Mo_6$ -type  $\mu$  phase and the EHEA (FCC + Intermetallic) exhibits compressive strength and plastic strain of 2364 MPa and 14.4 %, respectively. He et al. [116] reported the CoCrFeNiNb<sub>0.5</sub> EHEA, revealing eutectic microstructure consisting of FCC CoCrFeNi-rich solid solution phase and CoCrNb-type intermetallic and the alloy system shows balanced mechanical properties i.e., the compressive strength of 2300 MPa and fracture strain of 23.6 %. Huo et al.[81] reported the Zr-containing CoCrFeNiZrx (x=0.1, 0.2, 0.3, 0.4, and 0.5) EHEA consisting of FCC solid solution phase and C15 type Laves phase. It is found that CoCrFeNiZr<sub>0.4</sub> EHEA shows the highest strength of 667 MPa, while CoCrFeNiZr<sub>0.1</sub> EHEA shows highest 11 % ductility as compared to the other alloys system. In this study, it is observed that with increasing the amount of Zr, the volume fraction of the C15 Laves phase also increases and at x=0.5 fully eutectic microstructure is obtained (SEM images is given in **Fig. 1.26a, 1.26b**). TEM images for x=0.5 (as given in **Fig. 1.26c, 1.26d**) and selected area electron diffraction pattern (SAED) pattern of phase as marked as 'A' in the EHEA is shown in **Fig. 1.26e**.

Jiang et al. [116] reported the CoCrFeNbxNi HEAs. It is observed that the alloy with x=0 shows the microstructure having FCC solid solution phase, while the alloy with x=0.25, 0.45, 0.5, 0.75, 1.0 and 1.2 exhibits eutectic microstructure between FCC solid solution phase and Laves phase. It is observed that the alloy reveals hypoeutectic microstructure at x=0.25, fully eutectic at x=0.45, and finally hyper eutectic microstructure for other value of x. It is to be noted that fully eutectic alloy system at x=0.45 shows the highest compressive strength of 2558 MPa with fracture strain of about 27.9 %. The CoFeNb<sub>0.75</sub> Ni<sub>2</sub>V<sub>0.5</sub> EHEA is reported by Jiang et al. [117], and they observed the fully lamellar microstructure with FeCoNi-rich (FCC) solid solution phase and Fe<sub>2</sub>Nb-type Laves phase. The alloy shows the yield stress, compressive strength and plastic strain of 2073 MPa, 2232 MPa, and 3.4, respectively.



Fig. 1.26 SEM and TEM morphology CoCrFeNiZr<sub>0.5</sub> [81]

Zhang et al. [118] investigated CoCrFeNiNbx (x= 0.15, 0.3, and 0.45) hypoeutectic HEA and found that the minor addition of Nb increases the hardness from 297 HV to 500 HV and the YS from 300 MPa to 1115 MPa. Chanda et al. [100] reported the nano-eutectic CoCrFeNiNb<sub>0.5</sub> HEA consisting of FCC solid solution and Fe<sub>2</sub>Nb-type Laves phase with 134 nm interlamellar spacing (SEM micrograph for CoCrFeNiNb<sub>0.5</sub> HEA is shown in **Fig.1.27**). The alloy exhibits a YS of 2060 MPa, compressive strength of 2200 MPa, and a plastic strain of 17 %. In this study, the prediction of phase evolution and their stability is also accessed by VARIOUS thermodynamic parameters. It is found that the atomic size difference and electronegativity are successfully used to predict the coexistence of dual-phase FCC (or BCC) and TCP phase. The DTA (differential thermal analyzer) curve of CoCrFeNiNb<sub>0.5</sub> HEA

shows a single endothermic peak, (as shown in the inset of **Fig.1.27**), confirming eutectic melting temperature.



Fig. 1.27 SEM micrograph and DTA for CoCrFeNiNb<sub>0.5</sub> HEA [100]

Guo et al. [119] reported the CoCrFeMo<sub>0.8</sub>Ni EHEA consisting of FCC solid solution phase and Cr<sub>9</sub>Mo<sub>21</sub>Ni<sub>20</sub>-type intermetallic (as shown in Fig. 1.28a). The alloy exhibits a compressive strength of 2200 MPa, plastic strain of 7.5 % and hardness of 610 HV. The fracture surface after compression testing for EHEA reveals the quasi-cleavage type fracture (as shown in Fig. 1.28b). Jiang et al. [120] investigated CoCrFeNiTa<sub>0.4</sub> EHEA and reported that the microstructure of EHEA reveals the presence of FCC solid solution phase and Co<sub>2</sub>Ta-type Laves phases. It is found that the alloy system shows excellent fracture strength of 2293 MPa and plasticity of 22.6 % due to uniform lamellae structure. Huo et al. [121] reported the CoCrFeNiTa<sub>x</sub> (x=0.1, 0.2, 0.3, 0.395, 0.4, 0.5, x value in molar ratio) EHEA consisting of CrFe-rich FCC solid solution phase and Ta-rich Laves phase. EHEA with x=0.395 shows the good mechanical properties (i.e., yield strength of 1.4 GPa) which is due to the formation of dual-phase microstructure (SEM images of EHEA at x=0.395 is given in Fig.1.29a at low magnification, Fig.1.29b at higher magnification).



**Fig.1.28** (a) SEM image of CoCrFeMo<sub>0.8</sub>Ni EHEA as cast, (b) Fracture surface after Tensile testing [119]



**Fig.1.29** SEM images of EHEA at x=0.395 (a) low magnification (b) higher magnification [121]

## (ii) Microstructure and mechanical properties of (BCC+ Intermetallic) EHEAs

Ma et al. [105] studied the AlCoCrFeNbx EHEAs which reveals the microstructure varying from hypoeutectic to hypereutectic, consisting of BCC solid solution phase, and (CoCr)Nb type Laves phase. It is found that with the addition of Nb, the yield strength increases from 1373 MPa to 2473 MPa, whereas plastic strain decreases from 24.5 % to 4.1 %. The AlCoCrFeNb<sub>0.25</sub> EHEA shows 1959 MPa and 3008 MPa yield strength and ultimate strength, respectively, and fracture strain of 10.5 %. Wang et al. [122] reported novel bulk EHEA with excellent yield strength at elevated temperature and with a uniform and ultrafine consisting of lamellar microstructure between Laves phase L2<sub>1</sub> and BCC phases. The presence of BCC solid solution and Laves phases are confirmed by SEM analysis, EBSD analysis and XRD pattern (as shown in **Fig. 1.30a to 1.30e**). The DSC curve also indicates only one melting peak, corresponding to the eutectic composition (as shown in **Fig.** 

**1.30f**). **Fig. 1.31a** shows the variation of hot hardness with temperature, indicating the thermal stability at high temperature. **Fig. 1.31b** shows the engineering stress-strain plot of the designed EHEAs at different temperatures.



**Fig.1.30** (a) As-cast ingot, SEM micrograph at (b) low and (c) high magnification (d) XRD pattern (e) EBSD phase map (f) DSC curve of the as-cast AlCr<sub>1.3</sub>TiNi<sub>2</sub> EHEA ingot [122]



Fig. 1.31 (a) Comparison of hot hardness with other HEAs (b) Stressstrain curve at different temperatures [122]

# (iii) Microstructure and mechanical properties of (BCC+ FCC) EHEAs

Yong et al. [123] studied the AlCrFeMo<sub>0.2</sub>Ni EHEA, consisting of FeCrrich BCC solid solution phase, and AlNi intermetallic compound and EHEA exhibits 1487 MPa, 3222 MPa yield strength, and fracture strength, respectively. Li et al. [124] studied the AlTiCrxFeCoNiCu (x: molar ratio, x = 1.0) EHEAs, fabricated by vacuum arc melting technique and reported that HEAs consist of three phases, i.e., two FCC and BCC solid solution phases. EHEA consists of FCC (Ni, Al, Ti, Co) -rich ( $\alpha$ ) solid solution phase and BCC (Cr, Fe)-rich ( $\beta$ ) solid solution phase, showing the compressive strength of 1.42 GPa, and elongation of 5.68 %. Wani et al. [125] reported the AlCoCrFeNi<sub>2.1</sub> EHEA in as-cast conditions as well as at different thermomechanical processing conditions and observed that there is tremendous gain in mechanical properties in the different thermomechanical conditions. It is found that EHEA exhibits YS 620 MPa, UTS 1050 and plastic strain 17 % at ascast state respectively, while after 90 % cold-rolled condition, the YS and UTS of thermomechanical processed EHEA is found to be 625 MPa and 1800 MPa respectively with plastic strain 6 %. Ma et al. [126] reported the AlCrCuFeNi<sub>2</sub> EHEA having the eutectic microstructure consisting of FCC FeCr-rich solid solution phase and BCC AlNi-rich ordered phase. It is observed that EHEA shows the YS of 855 MPa, the fracture strength of 2123 MPa, and failure strain of 30 % at a 10<sup>-3</sup> s<sup>-1</sup> strain rate.

Hu et al. [127] performed the ceramic rolling (Al<sub>2</sub>O<sub>3</sub> granules act as pressure transmission medium during the cold rolling up to 23.06 % reduction in thickness) and annealing (400 °C and 800 °C) on AlCoCrFeNi<sub>2.1</sub>EHEA. After cold rolling, the YS, the compressive strength increases from 557.09 MPa to 1611 MPa, 1747.66 MPa to 2212.99 MPa respectively, while plastic strain decreases from 34 % to 28.6 %. It is observed that the EHEA with cold rolling and annealing at 400 °C shows the YS, compressive strength, and plastic strain 1330.12 MPa, 2055.46 MPa, and 33.72 % respectively. It is concluded that the strength of EHEA is improved due to the formation of multiple shear bands and uniform distribution of residual stress during the secondary processing.

Furthermore, Lu et. al. [128] reported large scale eutectic and neareutectic AlCoCrFeNix (x = 2.0, 2.1 and 2.2) EHEAs having L12 FCC and BCC B2 phases. The tensile test of EHEAs shows good combination of ductility and strength at different compositional and temperature ranges. Gao et al. [129] has reported an EHEA with the composition of AlCoCrFeNi<sub>2.1</sub> having a combination of ductile FCC (L1<sub>2</sub>) phase and brittle BCC (B2) phase with remarkable mechanical properties in which an excellent combination of UTS (1351 MPa) and ductility (15.4%) is observed. **Fig. 1.32a** reveals the presence of BCC and FCC phases. **Fig. 1.32b** shows the EBSD mapping of the AlCoCrFeNi<sub>2.1</sub>. The EBSD mapping confirms the presence of the FCC (L1<sub>2</sub>) phase and BCC (B2) phase (as shown in **Fig. 1.32**). The stress-strain curve of as-cast AlCoCrFeNi<sub>2.1</sub> EHEA is shown in **Fig. 1.32c;** indicating the excellent combination of UTS (1351 MPa) and ductility (15.4%).



Fig.1.32 (a) XRD pattern of EHEA (b) EBSD mapping of EHEA (FCC, BCC, phase boundaries and grain boundaries are marked in cyan, yellow, black and red colours respectively) (c) Stress-Strain curve of the EHEA [129]

# (iv) Microstructure and mechanical properties of (BCC + HCP) EHEAs

Rogal et al. [130] developed equiatomic Nb<sub>25</sub>Sc<sub>25</sub>Ti<sub>25</sub>Zr<sub>25</sub> EHEA consisting of the nano-scale lamellar eutectic between  $\alpha$  (Sc, Zr) HCP plates and  $\beta$ -NbZrTi with BCC phase. The balanced mechanical properties are observed due to dual-phase formation. The value of hardness, yield strength, compressive strength and plasticity are found to be 418 HV, 1020 MPa,1250 MPa and 8.2 %, respectively. Rogal et al. [131] reported the dual-phase EHEA consisting of BCC and HCP phases with nano precipitates of  $\omega$  phase and found that dual-phase EHEA exhibits high strength and good ductility. **Fig. 1.33a** shows the TEM image, revealing the presence of HCP and BCC phases. **Fig. 1.33b** shows the compressive stress-strain curve of the EHEA with the variation of Re, indicating excellent mechanical properties (UTS = 1910 MPa, YS = 1550 MPa, strain = 8% and Hardness = 516 ± 9 HV) for Sc<sub>13</sub>Ti<sub>30</sub>Zr<sub>30</sub>Hf<sub>25</sub>Re<sub>2</sub> EHEA.



**Fig.1.33** (a) TEM micrograph for  $Sc_{13}Ti_{30}Zr_{30}Hf_{25}Re_2$  EHEA (b) Compressive stress-strain curves for  $Sc_{25}Ti_{25}Zr_{25}Hf_{25}$ ,  $Sc_{13}Ti_{30}Zr_{30}Hf_{25}Re_2$ ,  $Sc_{10}Ti_{30}Zr_{30}Hf_{25}Re_5$  EHEAs [131]

#### (v) Microstructure and mechanical properties of Bimodal EHEAs

Jain et al. [132] designed and developed the CoCrFeNiZr bimodal EHEA, revealing two types of eutectics such as the globular eutectic and the lamellar eutectic (as shown in **Fig. 1.34a,1.34b**). It is also found that TEM micrographs (as given in **Fig. 1.34c**) show the fine scale microstructural features, indicating the presence of both globular and lamellar eutectics. The compressive true stress-strain curves (as shown in **Fig. 1.34d**) of the

bimodal EHEA show improved mechanical properties at high temperature.



**Fig.1.34** (*a*, *b*) SEM micrographs (*c*) TEM micrographs (*d*) Compressive true stress-strain curves of multicomponent (CoCrFeNi)<sub>90</sub>Zr<sub>10</sub> EHEA [132]

### (vi) Mechanical properties of EHEAs at elevated temperatures

Feng He et al. [66] have investigated five-component CoCrFeNiNb<sub>x</sub> (x = 0.5, 0.65 and 0.8) EHEA and observed the microstructural stability at elevated temperature up to 750 °C. The SEM micrographs of EHEA for X = 0.65 are shown in **Fig. 1.35**, indicating the microstructural stability at high temperature. The XRD pattern of EHEAs (as shown in **Fig. 1.36a**) shows the diffraction peaks corresponding to FCC and Laves phases, which indicates that the no phase transformation with the variation of annealing temperatures. **Fig. 1.36b** shows the variation of mechanical properties with the annealing temperatures and the different mechanical properties with the variation of annealing temperatures are given in **Table.1.3**. It is found that the compressive fracture strength of the EHEAs is approximately 2 GPa and exhibits the retention of strength high temperatures (as given in **Table 1.3**).



**Fig.1.35** SEM micrograph of CoCrFeNiNb<sub>0.65</sub> EHEA in (a) as cast state, Annealed for 24 hr at (b) 600 °C (c) 750 °C (d) 900 °C [66]



**Fig.1.36** (a) XRD pattern (b) stress-strain curve and hardness variation of annealed CoCrFeNiNb<sub>0.65</sub> EHEA at different temperature (600°C 750°C, 900°C) [66]

Recently, Han et al. [133] reported a novel equiaxed EHEA consisting of FCC solid solution phase and C14 Laves phase and found the high strength as well as good ductility at a temperature up to 800°C, i.e., YS of ~800 MPa and ductility of ~16%. The detailed analysis of the studied EHEA using XRD and SEM is shown in **Fig. 1.37**. **Fig. 1.38a** shows that the strain-softening is not observed for all the samples. The YS vs. elongation to fracture curve is shown in **Fig. 1.38b**. The linear relationship between yield strength and elongation is different than other HEAs and conventional eutectic alloys. This relationship shows the strength-ductility trade-off and their application for high temperature applications.

Alloys	Temperature	Yield	Fracture	Fracture
	(°C)	Stress	Stress	Strain
		(MPa)	(MPa)	(%)
CoCrFeNiNb <sub>0.5</sub>	600	1164.54	2207.1	24.2
	750	1031.45	2304.58	27.3
	900	1021.77	2142.2	25.8
CoCrFeNiNb <sub>0.65</sub>	600	1635.66	2392.64	14.3
	750	1407.65	2736.13	22.5
	900	1121.38	2320.12	23.5
CoCrFeNiNb <sub>0.8</sub>	600	1508.36	2357.05	11.5
	750	1377.39	2355.61	14.1
	900	1267.57	2119.43	13.4

 Table.1.3 Mechanical properties of Annealed novel designed

 CoCrFeNiNb<sub>X</sub> EHEAs [66]



**Fig.1.37** (a) XRD patterns of the gas-atomized powder, the as-extruded and different annealed EHEA samples, (b) Morphology of the gasatomized powder and the particle size distribution (inset), (c) Crosssection view of the gas atomized powder, (d) microstructure of the asheated EHEA, and (e) as-extruded [133]



**Fig.1.38** Engineering stress-strain curves for the as-extruded and subsequently annealed EHEA alloy tested at 800°C (*b*) comparison of *YS* as the function of elongation for presently studied EHEAs and other high-temperature alloys at 800°C [133]

# (vii) Comparison of EHEAs with other HEAs and conventional alloys

Tiwary et al. [134] reported the possibility of development of highstrength structural engineering materials using EHEAs based upon the yield strength vs. ductility plot of the available alloys of EHEAs (given in **Fig. 1.39a**). The comparison of mechanical properties of the ultrafine EHEAs with the conventional eutectic alloys, single-phase HEAs and bulk metallic glasses (BMGs) (as shown in **Fig. 1.39b**), indicating that EHEAs exhibit better mechanical properties as compared to other reported alloys. Chanda et al. [33] summarized the mechanical properties of conventional alloys and compared with eutectic alloys (as shown in **Fig. 1.40**). It is reported that the mechanical properties of nano or ultrafine eutectic depend on the length scale of eutectic colony and heterogenous crystalline phases.



Fig. 1.39 Comparision of the yield strength vs. plastic strain curve of EHEAs (a) with other EHEAs (b) with other conventional eutectic alloys [135]



Fig. 1.40 Comparision of mechanical properties of conventional alloys and EHEAs [33]

## 1.4.7 Hot deformation behaviour and processing maps of EHEAs

The manufacturing process of EHEAs can be designed by understanding the flow stress behaviour and the evolution of microstructural features during thermomechanical processing. Due to the fact that thermomechanical processing variables like temperature, strain rate, and strain during high temperature deformation affect the microstructure and therefore the properties. The investigation of flow stress behaviour during hot forming is required to develop for high-temperature applications of EHEAs. The processing maps of EHEA are generated to identify the stable region during thermomechanical processing. It is to be noted that the processing map is a required tool to find out the optimum condition and to describe the flow instability regions. The plastic deformation is studied at different strain rates and temperatures to develop a processing map and to understand the deformation behaviour of the investigated EHEAs. The processing maps has been generated with the help of dynamic material modelling (DMM) to understand the flow behaviour of EHEA. The DMM model assumes that the total energy absorb during the hot working can be divided into two parts. One part of the absorb energy is due to the rise in temperature or dissipation of energy during plastic deformation and the second part of the absorb energy is the energy which is related to the microstructure changes during processing. As a result, the total energy can be defined as

$$P = \sigma \dot{\epsilon} = \int_0^{\dot{\epsilon}} \sigma \, d\dot{\epsilon} + \int_0^{\sigma} \epsilon \, \dot{d}\sigma = E_P + E_M \tag{1.17}$$

The processing maps are constructed with the superposition of power dissipation efficiency ( $\eta$ ) and instability parameter ( $\xi$  ( $\dot{\epsilon}$ )). The  $\eta$  and  $\xi$  ( $\dot{\epsilon}$ ) can be defined as follows.

$$\eta = \frac{E_M}{E_{M_{max}}} = \frac{2m}{m+1} \tag{1.18}$$

$$\xi\left(\dot{\varepsilon}\right) = \frac{\partial ln \frac{m}{m+1}}{\partial ln \,\dot{\varepsilon}} + m \tag{1.19}$$

, where m is a strain rate sensitivity parameter which is a fundamental mechanical property and hot workability of the material can be affected by this parameter and is defined as

$$\mathbf{m} = \frac{d\sigma}{d\varepsilon} = \left(\frac{dE_M}{dE_P}\right)_{T,\epsilon} = \left(\frac{\partial \ln\sigma}{\partial \ln\varepsilon}\right)_{T,\varepsilon}$$
(1.20)

, where  $\sigma$  is the effective flow stress,  $\dot{\varepsilon}$  is represented by strain rate, T is the working temperature and  $\varepsilon$  is the strain.

The stability and instability conditions during the hot deformation analysis have been reported [136] and it is stated that the instability conditions are given as " $2m < \eta \le 0$ " and the stability conditions are " $0 < \eta \le 2m$ ". These both conditions are applicable for all isothermal hot deformation testing for every stress and strain values. One more parameter i.e., temperature sensitivity parameter (s) is defined which is necessary to identify the safe region for further mechanical processing during the hot deformation behaviour and is defined as

$$s = \frac{\partial \ln \sigma}{\partial \left(\frac{1}{T}\right)} \tag{1.21}$$

The following criteria for stable plastic flow are given below:

$$\dot{m} < 0$$
(1.22) $0 < m < 1$ (1.23) $s \ge 1$ (1.24) $\dot{s} \le 0$ (1.25)

, where  $\dot{s}$  and  $\dot{m}$  are the partial derivatives with respect to strain rate of s and m respectively and the expressions for  $\dot{s}$  and  $\dot{m}$  are given below:

$$\dot{s} = \frac{\partial s}{\partial \ln \dot{\epsilon}} \tag{1.26}$$

$$\dot{m} = \frac{\partial m}{\partial \ln \dot{\varepsilon}} \tag{1.27}$$

 $\xi$  ( $\dot{\epsilon}$ ),  $\dot{s}$  and  $\dot{m}$  are the function of temperature and strain rate and are used to plot the instability maps.

It is important to note that the processing map predicts the flow instability and regimes for safe processing. In general, the hot working processing of materials falls in the temperature range of 0.6-0.8 T/T<sub>m</sub> and strain rate range of 0.001- 100 s<sup>-1</sup>. Safe and unsafe zones during the hot working processing of materials are dependent on several atomistic mechanisms. The high-temperature processing of materials is mainly associated with mechanisms: the following (1)dynamic recrystallization, (2) superplastic deformation, (3) adiabatic shear band formation, flow localization, (4) wedge cracking, and (5) crystalline cracking. From the above mechanism of hot deformation, dynamic recrystallization is a safe process, superplastic deformation under controlled conditions is also safe, while all the remaining processes are considered as unsafe and hence should be avoided for developing the good product.

During the thermomechanical processing of materials, defects have been observed under certain processing conditions. These defects make the material thermodynamically unstable. But during the high-temperature deformation of materials, these defects need to be removed which is related to thermodynamically activated process [137]. By recovery phenomena, the microstructure is restored to some extent. If recovery is taken place by annealing, this is known as static recovery, while if recovery is taken place by deformation, then this is known as dynamic recovery. Store energy within the materials is the driving force for recrystallization. Recrystallization is a process in which the new grains form due to the lattice strain and crystalline imperfection during the deformation. It is to be noted that the hot deformation behaviour of HEAs at different temperatures and strain rates are investigated, so it is helpful to understand how the thermomechanical processing parameters affect the DRX. In general, if the processing temperature is high and the strain rate is low, multiple peaks are observed in the flow curve, while in the opposite case (low temperature and high strain rate) single peak in flow curve is observed. Apart from that, strain hardening and softening processes occur during the hot deformation of alloys. The strain hardening is observed due to the increase in dislocation density because of the external load and dislocation interaction (dislocation pileup). The softening was observed in the alloys due to a decrease in the dislocation density and redistribution of the dislocation (vacancy climb, formation of nuclei, and nuclei growth by migration of large-angle grain boundary) [138–140]. Microstructural evolution during the dynamic recovery and dynamic recrystallization is represented in Fig.1.41 [141].

Conventionally, DR process is associated with copper and nickel due to their SFE during hot deformation. These metals show flow softening behaviour after reaching the critical strain. At large strain, the flow curve reaches a steady-state, while oscillation in the flow curve is observed at lower strain rates. DR process is also understood by the nucleation and growth model, proposed by Luton [142], and that model considers both hardening (due to dislocation formation) and softening (due to grain boundary motion) effect.



**Fig.1.41** Microstructural evolution during the dynamic recovery and dynamic recrystallization [141]

The microstructure observation of different models may not be the same an actual dynamic condition due to the post deformation as recrystallization during colling. Here, the optimization of hot working parameters and control of microstructure during processing are the main aspects during thermomechanical processing of materials. In the literature, it is found that the DR is an essential mechanism for bulk metalworking. All aspects of this mechanism help in studying the hot deformation, including optimum conditions under which it occurs, strain dependence on DR, and microstructural changes during DR [138, 143]. The range of strain rate and temperature explain either the flow of materials is stable or unstable during the processing. At higher strain rates, the processing is done under the non-isothermal condition, and in this situation, the contact between the workpiece and die is very small. On the other hand, isothermal processing is required if the temperature range is narrow for DR or the strain rate is slow, and the material has a large domain of instability [144]. Rahul et al. [145] investigated the hot deformation behaviour of AlCoCrFeNi2.1 EHEA having FCC (CoCrFerich) solid solution phase and BCC (NiAl-rich) solid solution phase. The XRD plot and electron microscopy (SEM and TEM) micrographs of ascast alloy is presented in Fig.1.42.



**Fig.1.42** (a) XRD plot (b) BSE-SEM micrographs (c) TEM analysis of AlCoCrFeNi<sub>2.1</sub> EHEA [145]

Rahul et al. [145] generated the processing maps using the DMM model for AlCoCrFeNi<sub>2.1</sub> EHEA with different modelling parameters (as shown in **Fig. 1.43c to 1.43g**) to understand the hot workability of material at different thermomechanical conditions. **Fig. 1.43a and 1.43b** indicates that the flow stress increases with the increase in strain rate and the flow stress decreases with temperature. The SEM micrographs of the deformed samples at 1000 °C are shown in **Fig. 1.43h, 1.43i** which are at different strain rate of 0.001 S<sup>-1</sup> and 10 S<sup>-1</sup> respectively. These microstructures are correlated with the different regions of the processing maps. **Fig. 1.43h** shows the crack free uniform distribution in the stable region and **Fig. 1.43i** shows cracks, pores and adiabatic shear bending in the unstable region. It is concluded that the EHEA exhibits stable plastic flow in the range 1073-1150 K and  $10^{-3}-10^{-2.2}$  s<sup>-1</sup> as well as 1338-1373 K and  $10^{-3}-10^{-1.2}$  s<sup>-1</sup>.



Fig.1.43 (a, b) Stress-strain plot for EHEA at different temperatures and strain rates of 0.001 s<sup>-1</sup> & 10 s<sup>-1</sup> (c) processing maps at strain 0.6 (d) m
(e) ṁ (f) s (g) ṡ (h, i) SEM micrographs of deformed samples at 1000 °C and strain rates of 0.001 s<sup>-1</sup> & 10 s<sup>-1</sup> [145]

## **1.4.8 Potential Applications of EHEAs**

It is worthy to mention that EHEAs are considered as a potential structural material for high-temperature applications due to outstanding mechanical properties and easy processing. EHEAs can also be used for tools, dies, moulds, furnace parts etc which require high strength, thermal stability, oxidation and wear resistance, which can be widely used in propellers for ice breakers instead of stainless steel and copper alloys [146]. EHEAs are widely used in ships, motor housing, valves, offshore oil platform, pipelines due to their excellent mechanical properties at high temperatures and used as shock absorbers due to their excellent damping properties[146]. EHEAs can be used as high-temperature filler materials for seal materials in SOFCs. The EHEA Nb<sub>0.73</sub>CoCrFeNi<sub>2.1</sub> has been used as filler material or high temperature joint to braze crofer 22 APU to Hf metallized yttria-stabilized zirconia (as shown in **Fig. 1.44**) at 1200 °C due to the hardness of  $352 \pm 17$  HV and shear strength of the joint of  $97 \pm 7$ 

MPa and is found to be two times higher as compared to the other conventional alloys filler materials [147].



Fig. 1.44 Fractured YSZ-EHEA-Crofer sample [147]

#### 1.5 Research Gap and Motivation of thesis

A critical analysis of the available literature on the uses of Al alloy and development of novel Al alloys indicates that the requirement of superior mechanical properties, microstructure consisting of eutectic, peritectic and combination of both have not been fulfilled till now. The design of the eutectic Al alloys with a good balance between strength and ductility will be promising for room temperature and at elevated temperature. The available literature also indicates that there are still need to develop EHEAs with the combination of soft and hard phases for high strength and high temperature application. The phase equilibria study in the multicomponent alloys have not been explored up to the acceptable requirement till now. During the development of novel multicomponent alloys specially in case of HEAs, it is necessary to identify the hot workability regions and high temperature properties. On the base of available literature and to the best of the authors' knowledge, neither the modelling for vacuum arc melting cum suction casting approach nor any solidification simulations of HEAs have been published till now. Additionally, research related to the prediction of hot deformation behaviour utilizing the different models (phenomenological, physicsbased, and ANN-based model) for HEAs is also limited.

## **1.6 Objectives**

On the base of above literature review and research gap, the primary objectives of the present thesis are listed as given below to fulfil the research gap:

- I. To design and develop novel Al based multicomponent alloys to investigate the effect of alloying elements on the mechanical and tribological behaviour of the Al alloys by using integrated approach.
- II. To develop a solidification simulation model and its experimental validation of high entropy alloys and eutectic high entropy alloys by using ANSYS Fluent software.
- III. To design and develop FeCoNiCrVAl single phase HEA, 6 component FeCoNiCrVTa EHEAs, 7 component FeCoNiCrVAlTa EHEAs by thermodynamic simulation and experimental approach.
- IV. To generate the processing maps using multiple models to identify the hot workability regimes of developed HEAs.
- V. To predict the flow curves at different strain rates and temperatures of HEAs using different models and ANN approach.

## **1.7 Thesis Structure**

The thesis outlines to fulfil the above-mentioned primary objectives are summarized in the following sections:

**Chapter 1** is the introductory chapter, which describes the background, motivation, and goals of the current work and presents the comprehensive review of literature on different aspects of Al based alloys. solidification simulation of multicomponent alloys and on the different aspects of HEAs which leads to the foundation of the current thesis.

**Chapter 2** describes the experimental methodologies associated with the synthesis of alloys and characterization techniques used in the present work.

**Chapter 3** deals with the design and development of Al based multicomponent alloys with the evolution of different phases to investigate the effects of Fe, Cr, Co, V, Ta and Si on Al-Ni system and Si and Ni on Al-Cu system.

**Chapter 4** deals with the design and development of single phase HEAs by using ICME approach.

**Chapter 5** deals the hot deformation behaviour of 6 component single phase FCC HEA.

**Chapter 6** describes the design and development of EHEAs by using ICME approach.

**Chapter 7** contains the overall conclusions of the present thesis and the scope for future work.

## Chapter 2

## Work Plan and Methodology

This chapter describe the work plan of the present thesis in detail to complete the objectives with integrated approach such as Numerical approach and Experimental approach. It describes the strategy and methodology to design and develop the novel multicomponent alloys/high entropy alloys. In the end of chapter, the complete work plan to complete the desired goals is summarized in the flow chart. Only the most basic or important components of numerical techniques and experiment methods are covered in this chapter and the specific details about the experiment methodology involved in the specific study are mentioned in the respective chapters.

# 2.1 ThermoCalc simulation to design and select the alloy composition

The thermodynamic simulation approach was used to design the multicomponent alloys/high entropy alloys to predict the evolution of phases solidification with the help of ThermoCalc® software using the TCHEA2® database. ThermoCalc software is widely used to predict the solidification pathways and possible number of phases during the solidification and therefore evolution of the microstructure. On the base of these results, we can select a particular composition to obtain the appropriate microstructure and excellent mechanical properties at room temperature as well as elevated temperature. Using the ThermoCalc software, Isopleth phase diagram, scheil's solidification curve and amount of phases vs. temperature plot etc were plotted.

## **2.2 Materials**

For the development of novel multicomponent alloys, materials are used in highly purity form that is more than 99.9 % pure metals. Pure elements (Fe, Co, Cr, V, Ta, Mo, Al, Cu, Ni & Si) were used to develop the alloys. Al with 99.99% purity containing 8mm diameter road was used to melt in the arc melting unit. With the pure Al, Cu with purity level 99.99% in the rod shape of 30mm diameter was used. Si with a 99.9 % purity level in the lumps form was used. Ni with a 99.8% purity level in the rectangular form with the size of 50mm length and 20mm width was used to make the alloys. Fe was in the form of pieces with a size of around 25 mm in irregular shapes with a purity level of 99.97%. Cr was in the form of pieces of irregular shapes with a purity level of 99.9%.

#### 2.3 Fabrication of Multicomponent alloys

The different multicomponent alloys were prepared by using different type of casting units.

#### 2.3.1 Vacuum arc melting (VAM) unit

An arc can be used to melt metals, mainly to create alloys. An electric arc is generated when a tungsten electrode contacts metals in a depression (crucible) in the copper hearth. During vacuum arc melting, the chamber is evacuated and subsequently filled with argon gas. As a result, melting occurs in an argon atmosphere. The basic principle of the arc melting is to generate the heat in the chamber to melt the elements and solidify with the help of chiller unit. The power supply is a typical Tungsten Inert Gas (TIG) welding equipment. The metals in the crucible melt due to the heat produced by the electric arc between the electrode and the metals, producing an alloy. To improve the alloy's homogeneity, it is melted several times. The vacuum arc melting (VAM) unit (as shown in **Fig. 2.1**) is the group of three parts:

**Vacuum Unit:** A turbo-molecular and roughing pump is used to create vacuum in a vacuum chamber, resulting in a pressure of around  $10^{-6}$  Torr. It has pneumatic control switches that are powered by a 2 HP compressor. Metals which are placed in a water-cooled copper-hearth plate are melted with a tungsten electrode in the vacuum chamber. A direct current is employed to create the arc in the presence of an argon environment. The arc length is defined as the distance between the electrode tip and die. It's worth noting that during melting, the distance

between the electrode tip and the die should be kept constant, and the electric arc is maintained by a DC power source connected to the electrode and the die.

**Welding Unit:** A standard Tungsten Inert Gas (TIG) welding unit is used as a power source (maximum voltage is 30V and current is 400 Amp). A non-consumable tungsten electrode is used to melt the metal.

**Chiller Unit:** The cold circulation water from the chiller cools both the copper hearth and the electrodes which is useful to obtain the high cooling rate during the deformation.

## 2.3.2 Suction Casting unit

Apart from the abovementioned parts and procedure, suction casting is one of the useful units to form an alloy with high cooling rate compare to the arc melting unit. It is also a part of arc melting but different copper hearth crucible (as shown in **Fig. 2.1**) is used with the creation of suction from bottom of the crucible. The alloys in cylindrical form or rectangular form can be obtained with the help of suction casting.



Fig.2.1 Experimental setup of complete VAM and suction casting unit

## 2.4 Characterization of multicomponent alloys

#### 2.4.1 Specimen Preparation

For various experiments, the specimens were cut by utilising Wire-cut EDM. The cross-section of specimens was hot mounted using Bakelite

powder for microstructural studies. Such mounted specimens were ground and polished using SiC emery paper up to 2500 mesh size, then polished with alumina and diamond paste (up to 0.25 m size). These polished samples were cleaned with the help of ultrasonicator by using acetone.

## 2.4.2 X-Ray Diffraction

The X-ray diffraction analysis was performed on polished specimens to investigate the presence of different phases via Panalytical Empyrean X-ray Diffractometer which is used with a Cu radiation target and operating at 45 kV and 30 mA with the step size of  $2\theta = 0.026$  and  $2\theta$  value varied from 10° to 100°. The diffraction patterns were analysed with the help of X-pert pro software. The setup used for XRD is shown in **fig. 2.2a**.

#### 2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

The prepared specimens were etched using Keller's etchant and Aqua regia etchant for 10-15 sec according to the type and nature of alloy. The microstructural characterization of the polished specimens was carried out with the help of FESEM equipped with energy dispersive spectroscopy (EDS) by using JEOL, JSM-7610 Fplus model (as shown in **fig. 2.2b**). SEM micrographs were recorded using secondary electron (SE) and backscattered electron (BSE) mode at 15 kV and 20 kV accelerating voltage. The information about the elements at a particular point or area was collected with the help of EDS analysis by taking atleast 5 points.



Fig. 2.2 Experimental setup for (a) XRD (b) FESEM

#### 2.4.4 Electron Back Scattered Diffraction (EBSD) analysis

The polished specimens need more preparation for EBSD analysis. The specimens were prepared by polishing up to 2500 mesh size emery paper followed by diamond polishing with 0.5  $\mu$ m paste for 20 mins and then final polishing was completed by using standard colloidal silica suspension for 1 hour. The EBSD analysis of the prepared samples were carried out by using JEOL JSM-7610 Fplus SEM containing EBSD detector. All the measurement were carried out at 20 kV acceleration voltage, 10 mA current density.

#### 2.4.5 Differential Scanning calorimetry (DSC) analysis

The DSC analysis was carried out using the Simultaneous Thermal Analyzer (Model: STA 8000) for all investigated alloys (as shown in **fig. 2.3a**). The endothermic and exothermic peaks can be observed from the DSC curve in the phase transformation process during the melting and solidification process or heating and cooling process. In the DSC experiments, the samples were kept in the closed graphite crucible. The average sample size which was used for the DSC analysis is 3 mm diameter and 2 mm thickness with an average weight is approx. 20 mg. The heating temperature range is from 29 °C to 650 °C with a heating rate of 5 °C/min and the cooling temperature range is from 650 °C to 29 °C with a cooling rate of 5 °C/min. The whole test was conducted in the inert atmosphere of pure argon gas. DSC analysis with the microstructural characterization is helpful to investigate the phase transformation behaviour and phase equilibria study.



Fig. 2.3 Experimental setup for (a) DSC (b) Microhardness

## 2.5 Mechanical testing of developed multicomponent alloys

## 2.5.1 Tensile testing

The tensile properties were measured using a universal testing machine (UTM) by following the ASTM E8 standard. The setup which was used for the testing are shown in **fig 2.4**. A constant crosshead speed of 0.75 mm/ min was used for the testing.



Fig. 2.4 Experimental setup for universal testing machine (UTM)

## 2.5.2 Micro Hardness

A micro-hardness test was conducted on the given studied alloys and hardness values were obtained with the help of Vickers micro-hardness tester (Model: MMV-A) (as shown in **fig. 2.3b**). A constant load of 100 gf was applied on the polished sample with the indentation speed of 26  $\mu$ m/s and the dwell time of 15 sec for each sample. 10 readings were taken for each sample in the longitudinal and transverse direction and average hardness for each alloy was calculated with the standard deviation.

## 2.5.3 Hot Deformation analysis

The isothermal hot compression tests of HEAs were carried out using the Gleeble 3800 thermo-mechanical simulator with hydrawedge module at various temperatures and strain rates. The cylindrical specimen was employed, with a diameter of 6 mm and an aspect ratio of 1.5:1. The cylindrical specimen was distorted to a height reduction of approximately 50%.

#### 2.6 Tribological Properties

To investigate the wear behaviour of studied alloys, fretting wear experiments were performed at different loads using a pin on flat type fretting wear tester (Model: DUCOM). The specimens for the wear testing were prepared using wire electrical discharge machining (WEDM) in the cubical shape with the dimensions of  $15 \text{ mm} \times 15 \text{ mm} \times 5 \text{ mm}$ . A standard counterpart material (EN-31 steel) with the dimensions of 15 mm height and 6 mm diameter was used to perform the wear testing of the prepared specimens. The different parameters such as amplitude, load, frequency, temperature, No. of cycles etc were mentioned in the respective chapters. To evaluate the wear volume loss during the wear testing, the specimens were cleaned properly in an ultrasonic bath after each test. **Table 2.1** lists the various parameters that are used during fretting wear testing. The wear volume loss during the fretting wear testing can be calculated by using the following equations [148]:

$$V = \frac{\pi h^2}{3} \left( 3R - h \right) \tag{1}$$

, where V is the volume loss in mm<sup>3</sup>, h is the wear scar depth, R is the radius of curvature of fretting area and can be calculated by following equation

$$R = \frac{d_1 d_2}{8h} + \frac{h}{2}$$
(2)

, where  $d_1$  and  $d_2$  are the length and width of wear scar along and perpendicular of fretting direction, respectively.

Parameters	Value			
Amplitude	250 μm			
Load	5 N, 10 N, and 15 N			
Frequency	30 Hz			
Temperature	Room temperature			
No. of cycles	54,000			

*Table 2.1*: *Testing parameters for fretting wear testing* 

### 2.7 Numerical analysis using ANSYS Fluent

The solidification simulation analysis was done by using computational fluid dynamic (CFD) approach. The CFD approach is available in ANSYS Fluent software and it is widely used to simulate the solidification phenomena. The investigation of the solidification behaviour, temperature distribution within the metal casting as well as the interface between the metal casting and the mould, and phase change during solidification were explored by simulation of the solidification process. The complete analysis about the phase change mechanism and variation of cooling rates were analysed with the help of cooling curve obtained from the simulation results.

## Chapter 3

# Design and development of Al based multicomponent alloys

#### **3.1 Introduction**

The present chapter aims to understand the solidification pathways of Al-based alloys with ultrafine eutectic with micron-scale dendrite. Among the binary eutectics, some of the most extensively studied eutectics are Al-Al<sub>2</sub>Cu, and Al-Al<sub>3</sub>Ni. Al-Al<sub>3</sub>Ni eutectics exhibit rod morphology with fibers of intermetallic phases embedded in Al matrix. On the other hand, the growth morphologies for Al-Al<sub>2</sub>Cu eutectic are different and consist of an alternate lamella of Al<sub>2</sub>Cu in Al matrix. These eutectics show good mechanical properties due to the presence of hard intermetallic phases that impede the dislocation motion and, hence, impart strength [17].

The Al-Ni and Al-Cu systems are widely used because they are important alloy systems that provide desirable properties to aluminum, such as increased strength, corrosion resistance, and heat resistance [149]. In the Al-Ni system, the addition of nickel to aluminum can improve strength, ductility, and thermal stability. Aluminum-nickel alloys are commonly used in aerospace applications because of their high strength-to-weight ratio, resistance to corrosion, and ability to retain their mechanical properties at high temperatures [19, 20]. In the Al-Cu system, the addition of copper to aluminum can improve strength, hardness, and corrosion resistance. Aluminum-copper alloys are commonly used in the automotive industry for engine parts, such as cylinder heads and pistons, because of their excellent thermal conductivity and ability to withstand high temperatures [20].

Overall, the Al-Ni and Al-Cu systems are widely used because they allow for the production of lightweight, strong, and corrosion-resistant aluminum alloys that are well-suited for a wide range of applications in various industries. It is observed by the research community that Al-Cu, Al-Ni alloys with the addition of alloying elements are expected as a good choice to enhance the strength and can be considered as potential for high temperature as well as high strength applications in the aerospace industry because of their excellent thermal stability.

The effects of different alloying elements (Fe, Cr, Co, V, Ta & Si) on the Al-Ni-X alloys and effect of Si & Ni on the Al-Cu-X alloys have been systematically investigated. Eutectic and near eutectic cast alloys after the addition of different alloying elements have been synthesized with the help of a vacuum arc melting unit. The solidification behaviour of the studied alloy was predicted by thermodynamic simulation using the ThermoCalc software and compared with experimental results. The thermodynamic simulation was performed to understand the formation of phases during solidification using the thermo-calc software (CALPHAD approach). Furthermore, the structural analysis of the alloys was carried out using the X-Ray Diffraction (XRD) technique, and the microstructure was examined using scanning electron microscopy (SEM) with electron dispersive spectroscopy (EDS) to identify the phases and track their evolution during the solidification process. Mechanical properties and thermal study have been done using the UTM, microhardness tester and differential scanning calorimeter (DSC). The main objective of the present chapter is to evaluate the effect of alloying elements on Al based multicomponent alloy with the design and development of new lightweight multicomponent alloys with unique microstructure as well as superior mechanical and good wear resistance properties. The mechanical properties of the studied alloy are better than other Al-based conventional alloys.

From the Al-rich region of Al-Ni binary phase diagram [150] (as shown in **Fig. 3.1a**), there are a peritectic reaction i.e., Al (L) + Al<sub>3</sub>Ni<sub>2</sub> $\rightarrow$ Al<sub>3</sub>Ni at 854°C and one eutectic reaction i.e., Al (L)  $\rightarrow$ (Al)<sub>ss</sub>+ Al<sub>3</sub>Ni at 639.9°C. While in Al-rich region of Al-Fe phase diagram [150] (as shown in **Fig. 3.1b**), there is one eutectic reaction i.e., Al (L)  $\rightarrow$ (Al)<sub>ss</sub>+ Al<sub>3</sub>Fe at 652°C. It is also found from Fe-Ni phase diagram [150] (as shown in **Fig. 3.1c**) that Fe is soluble in Ni to large extent i.e.,
nearly up to 90 at. %. The solidification behaviour of multicomponent Al-Ni-Fe alloy chosen for this study has been understood based upon the respective binary phase diagrams. Similarly, the phase evolution of other designed multicomponent alloys with the addition of different alloying elements (Cr, Co, V, Ta, Si) in Al-Ni system and the addition of Si and Ni in Al-Cu system have been understood by considering respective binary phase diagrams [150]. By following the same approach, other Al-Ni-X (X = Cr, Co, V, Ta, Si) alloys and their composition have been choosen.



**Fig. 3.1:** Selection approach of alloying elements using the phase diagrams of (a) Al-Ni, (b) Al-Fe and (c) Fe-Ni systems [150].

#### **3.2 Objectives**

- To design and develop novel multicomponent alloys using different alloying elements by integrated approach of combining thermodynamic simulation and solidification processing technique.
- To investigate the phase equilibria study experimentally and compared with the thermodynamic simulation.
- To investigate the mechanical behaviour at room temperature and at elevated temperatures as well as the wear resistance properties of the Al rich alloy with different alloying elements.

#### **3.3 Simulation and experimental procedures**

The prediction of phase evolution and solidification pathways were carried out by thermodynamic simulation using ThermoCalc software. The solidification behaviour of the investigated multicomponent alloys was done using Scheil solidification simulation under nonequilibrium condition. The computation of the phase evolution was done, and the composition of the investigated alloys was selected by generating phase diagram using ThermoCalc software [151, 152]. The investigated alloys ingots with the addition of different alloying elements were prepared by vacuum arc melting cum suction casting unit. For this purpose, pure elements were used to produce the investigated alloys. Al, Ni, Fe, Cr, Co, V, Ta, Cu and Si with the purity level of 99.9% were used in the form of shots of 9.5mm diameter in spherical shape, square block of 26\*26 mm<sup>2</sup>, pieces of 25 mm in irregularly shaped, pieces in irregular shaped, Coin shape, rectangular block, rod of 8mm diameter, irregular shape of balls and lumps forms respectively to produce the designed alloys. Using the given elements, different multicomponent alloys were developed with the selected nominal chemical composition of the developed alloys. An electronic weight balance system with the resolution of 0.001 g was used to weigh samples with nominal composition and then the elements were melted by using the vacuum arc melting unit using button shaped copper hearth plate. These alloys were remelted at least 5 times by altering the side each time to obtain the chemical homogeneous alloys. After that, the button is suction casted using a split type of copper mould. The whole casting procedure was completed in an inert atmosphere of argon gas to exclude the possibility of oxide layers and other contaminants.

Using the Panalytical Empyrean X-ray diffractometer, the X-ray diffraction (XRD) of the studied alloys was carried out to determine the presence of phases. The working conditions were 45 kV and 30 mA with a step size of  $2\theta = 0.026$  and  $2\theta$  value ranging from 10° to 100°. After that, the samples were prepared to visualize the microstructure of the developed alloys by following the standard procedure of cutting, mounting, and polishing samples. Keller's etchant is used to etch the

polished samples for 15 sec. The microstructures of the developed alloys were observed using the FE-SEM (JEOL, JSM-7610 Fplus) in back scattered electrons (BSE) mode. The composition of the different phases was identified by electron dispersive spectroscopy (EDS) analysis. The differential scanning calorimetry (DSC) analysis with a heating and cooling rate of 5 °C/min was conducted using a high temperature simultaneous thermal analyzer (Model: STA 8000) for all investigated alloys. The phase transformation behaviour can be investigated using DSC analysis by observing the endothermic and exothermic peaks. A closed graphite crucible was used to keep the samples during testing and the sample having approx. 20 mg weight was used. The DSC of all samples was conducted in an inert atmosphere of argon gas. It is to be noted that the DSC analysis is very important to investigate the solidification behaviour and phase equilibria study.

The effect of alloying elements on the mechanical properties of investigated alloy was examined using tensile testing and microhardness testing equipment. The tensile properties of the given alloys were measured using a universal tensile machine (UTM) by following the ASTM standards. A constant crosshead speed was used during the testing. A Vickers micro hardness tester was used to investigate the effect of alloying elements on hardness of multicomponent alloy. For each alloy, a constant load of 100 gf was subjected to the polished sample with an indentation speed of 26 m/s and a dwell period of 15 sec. For each sample, 10 readings were taken, and then average value of hardness was calculated with the standard deviation. The dry fretting wear experiments were conducted at room temperature with various loads utilizing a pin on flat type fretting wear tester using the DUCOM Model with the help of Win-Ducom 2010 software. The wire electrical discharge machining (WEDM) was used to prepare the specimens for wear testing, which were cubical in shape and were 15mm x 10mm x 5mm. The wear testing of the prepared specimens was carried out using a standard counterpart material (EN-31 steel) with dimensions of 15 mm height and 6 mm diameter.

# 3.4 Results and Discussion

#### 3.4.1 Thermodynamic simulation

To investigate the solidification pathways during the solidification and microstructure evolution, isopleth phase diagram is used which was calculated for the studied alloys using ThermoCalc software as shown in **fig. 3.2 and 3.3**. **Fig. 3.2** shows the evolution of different phases with the effect of different alloying elements (Fe, Cr, Co, V, Ta and Si) on Al-Ni system whereas **Fig. 3.3** shows the evolution of different phases with the effect of different alloying elements (Ni and Si) on Al-Cu system.



Fig. 3.2 Isopleth phase diagrams with the effect of alloying elements

(a) Fe (b) Cr (c) Co (d) V (e) Ta (f) Si on Al-Ni system.



Fig. 3.3 Isopleth phase diagrams with the effect of alloying elements (a) Ni (b) Si on Al-Cu system.

During the solidification, mole faction of phases with the variation of temperature is also computed with the help of ThermoCalc software. **Fig. 3.4 and 3.5** show the amount of phases *Vs*. temperature curves for different composition. **Fig.3.4 and 3.5** shows the formation of different phases in a sequence.



**Fig.3.4** Plot between the amount of phases vs temperature with the effect of alloying elements (a) Fe (b) Cr (c) Co (d) V (e) Ta (f) Si on Al-Ni system.

To investigate the solidification pathways during the solidification and microstructure evolution, the scheil's solidification curve is used which was calculated for the studied alloys using ThermoCalc software as shown in **fig. 3.6 and 3.7**. **Fig. 3.6** shows the evolution of different phases with the effect of different alloying elements (Fe, Cr, Co, V, Ta and Si) on Al-Ni system whereas **Fig. 3.7** shows the evolution of different phases with the effect of different alloying elements (Ni and Si) on Al-Cu system.



**Fig.3.5** Plot between the amount of phases vs temperature with the effect of alloying elements (a) Ni (b) Si on Al-Cu system.

In Al<sub>98.6</sub>Ni<sub>0.5</sub>Fe<sub>0.9</sub> alloy (as shown in Fig. 3.6a), First of all, Al<sub>3</sub>Fe phase formation starts at 935 K. After that at 923 K, a eutectic reaction (L  $\rightarrow$  $Al_3Fe + Al_{ss}$ ) starts and after that the remaining liquid solidifies with another eutectic reaction ( $L \rightarrow Al_{ss} + Al_9FeNi$ ) at 865 K. Fig.3.6b shows the formation of different phases for Al<sub>92</sub>Ni<sub>4</sub>Cr<sub>4</sub> alloy. First of all, Al<sub>7</sub>Cr phase formation starts at 1161 K. After that at 893 K, a Al<sub>3</sub>Ni phase formation takes place and then the remaining liquid solidifies with a binary eutectic reaction (L  $\rightarrow$  Al<sub>3</sub>Ni + Al<sub>ss</sub>) at 863 K. Fig. 3.6c shows the formation of different phases for Al<sub>92</sub>Ni<sub>4</sub>Co<sub>4</sub> alloy. First of all, a primary FCC\_A1 solid solution phase formation starts at 854 K. After that at 852 K, a eutectic reaction (L  $\rightarrow$  FCC\_A1 + FCC\_L12) occurs and finally the remaining liquid solidifies with another eutectic reaction  $(L \rightarrow BCC\_B2 + FCC\_A1)$  at 713 K. Fig. 3.6d shows the formation of different phases for Al<sub>93</sub>Ni<sub>4</sub>V<sub>3</sub> alloy. First of all, a primary BCC\_A2 solid solution phase formation starts at 967 K. After that at 965 K, another FCC\_A1 phase formation takes place and finally the remaining liquid solidifies with another eutectic reaction (L  $\rightarrow$  BCC\_B2 + FCC\_A1) at 873 K. Fig. 3.6e shows the formation of different phases for Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy. First of all, a laves phase formation starts at 1298 K. After that at 920 K, another FCC\_A1 phase formation takes place and finally the remaining liquid solidifies with an eutectic reaction (L  $\rightarrow$  FCC\_A1 + FCC\_L12) at 873 K. Fig. 3.6f shows the formation of different phases for Al<sub>84</sub>Ni<sub>4</sub>Si<sub>12</sub> alloy. First of all, a primary FCC\_A1 phase formation starts at 843 K. After that at 828 K, a eutectic reaction  $(L \rightarrow FCC_A1 + DIAMOND_A4)$  takes place and finally the remaining

liquid solidifies with a ternary eutectic reaction (L  $\rightarrow$  DIAMOND\_A4 + FCC\_A1 + FCC\_L12) at 873 K.



**Fig. 3.6** Scheil's solidification curves with the effect of alloying elements (a) Fe (b) Cr (c) Co (d) V (e) Ta (f) Si on Al-Ni system.

**Fig. 3.7a** shows the formation of different phases for Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloy. First of all, a primary FCC\_L12 solid solution phase formation starts at 854 K. After that at 851.8 K, a binary eutectic reaction starts with  $(L \rightarrow \alpha$ -Al + Al<sub>7</sub>Cu<sub>4</sub>Ni) which confirms the formation of the intermetallic phase. Finally, at 819.5 K, a ternary eutectic reaction starts with  $(L \rightarrow \alpha$ -Al + Al<sub>7</sub>Cu<sub>4</sub>Ni + Al<sub>2</sub>Cu), and the remaining liquid is completely solidified. **Fig. 3.7b** shows that the solidification starts at 835 K with the formation of primary solid solution phase and after that eutectic reaction  $(L + \alpha$ -Al  $\rightarrow$  Al<sub>2</sub>Cu) takes place at 797 K and after that a ternary eutectic reaction  $((L \rightarrow \alpha$ -Al + Al<sub>2</sub>Cu +  $\beta$ -Si)) takes place at 794.7 K from the remaining liquid.



Fig. 3.7 Scheil's solidification curves with the effect of alloying elements (a) Ni (b) Si on Al-Cu system.

# 3.4.2 Phase Equilibria study of designed multicomponent alloys

# 3.4.2.1 Structural characterization

The patterns of the as-cast Al-Ni-X (X = Fe, Cr, Co, V, Ta, Si) and Al-Cu-X (X = Ni and Si) ternary alloys obtained from XRD is given in **Fig.** 3.8. The identification of the peaks confirms the phases which are available in the studied alloys and the same phases as suggested by ThermoCalc software. The pattern obtained from XRD for Al<sub>98.6</sub>Ni<sub>0.5</sub>Fe<sub>0.9</sub> alloy expresses the existence of FCC (Al)<sub>ss</sub>, Al<sub>3</sub>Fe and tetragonal Al<sub>9</sub>FeNi phases. While FCC (Al)<sub>ss</sub> and orthorhombic Al<sub>3</sub>Ni and Al7Cr phases have been identified in the XRD pattern obtained of Al<sub>92</sub>Ni<sub>4</sub>Cr<sub>4</sub> alloy. The XRD pattern for Al<sub>92</sub>Ni<sub>4</sub>Co<sub>4</sub> alloy shows the existence of FCC (Al)ss, orthorhombic Al<sub>3</sub>Ni and Al<sub>8</sub>(Co, Ni)<sub>2</sub> phases while FCC (Al)ss and orthorhombic Al<sub>3</sub>Ni and Al<sub>3</sub>V phases have been identified in the XRD pattern obtained of Al<sub>93</sub>Ni<sub>4</sub>V<sub>3</sub> alloy. The XRD pattern for Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy shows the existence of FCC (Al)<sub>ss</sub>, Al<sub>3</sub>Ni<sub>2</sub>, Al<sub>7</sub>Ni<sub>3</sub>, Al<sub>3</sub>Ta and Al<sub>5</sub>Ta<sub>3</sub>Ni<sub>2</sub> phases while FCC (Al)<sub>ss</sub> and orthorhombic Al<sub>3</sub>Ni and Al<sub>3</sub>Si phases have been identified in the XRD pattern obtained of Al<sub>84</sub>Ni<sub>4</sub>Si<sub>12</sub> alloy.

The XRD pattern for  $Al_{88.5}Cu_{10}Ni_{1.5}$  alloy shows the existence of FCC (Al)<sub>ss</sub>, Al<sub>2</sub>Cu, and Al<sub>7</sub>Cu<sub>4</sub>Ni phases while FCC (Al)<sub>ss</sub>, Al<sub>2</sub>Cu and Si solid solution phases have been identified in the XRD pattern obtained of  $Al_{85}Cu_{10}Si_5$  alloy.



**Fig. 3.8:** XRD pattern of (a) Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) and (b) Al-Cu-X (X = Ni and Si) alloys.

#### 3.4.2.2 Microstructural characterization

The detailed microstructural characterization of the studied Al-Ni-X (X = Fe, Cr, Co, V, Ta, Si) and Al-Cu-X (X = Ni and Si) ternary alloys have been achieved using scanning electron microscopy (SEM) attached with energy dispersive spectroscopy (EDS) which are shown in Fig. 3.9 and Fig. 3.10. The characteristic SEM images of the designed ternary alloys are given here to decipher various phases in the microstructure. The altered phases in the microstructure are noticeable depend upon compositional measurement and Z-contrast. The SEM micrograph of Al<sub>98.6</sub>Ni<sub>0.5</sub>Fe<sub>0.9</sub> alloy is given in **Fig. 3.9a**, which confirms the existence of (Al)<sub>ss</sub> phase with grey contrast, Al<sub>9</sub>FeNi phase with bright contrast and Al<sub>3</sub>Fe with intense bright contrast. It is found that there are two eutectics microstructure with different morphologies i.e., lamellar eutectic between (Al)ss and Al9FeNi phases and globular eutectic between (Al)ss and Al<sub>3</sub>Fe phases. Fig. 3.9b shows the SEM micrograph of the Al<sub>92</sub>Ni<sub>4</sub>Cr<sub>4</sub> alloy which indicates the presence of Al<sub>7</sub>Cr phase (grey contrast), Al<sub>3</sub>Ni phase (bright contrast) and (Al)<sub>ss</sub> phase (dark contrast). It is observed that there are two dendritic phases of Al<sub>7</sub>Cr and Al<sub>3</sub>Ni and one ternary eutectic among (Al)<sub>ss</sub>, Al<sub>7</sub>Cr and Al<sub>3</sub>Ni phases. It is to be noted that Al<sub>7</sub>Cr phase is partially surrounded by Al<sub>3</sub>Ni phase, indicating Al<sub>3</sub>Ni phase is formed by peritectic reaction between liquid and Al<sub>7</sub>Cr phases. Fig. 3.9c shows the SEM micrograph of the Al<sub>92</sub>Ni<sub>4</sub>Co<sub>4</sub> alloy which indicates the presence of Al<sub>8</sub>(Co, Ni)<sub>2</sub> phase (bright contrast) and (Al)<sub>ss</sub> phase (dark contrast). One binary eutectic rection among (Al)<sub>ss</sub> phase and Al<sub>3</sub>Ni phase is also observed which is a very fine eutectic phase as shown in Fig. 4c. The SEM micrograph of Al<sub>93</sub>Ni<sub>4</sub>V<sub>3</sub> alloy is given in **Fig. 3.9d**, which confirms the existence of (Al)<sub>ss</sub> phase with dark contrast, Al<sub>3</sub>Ni phase with bright contrast and Al<sub>3</sub>V with grey contrast. It is observed that there are two dendritic phases of Al<sub>3</sub>V and Al<sub>3</sub>Ni and one ternary eutectic among (Al)<sub>ss</sub>, Al<sub>3</sub>V and Al<sub>3</sub>Ni phases. **Fig. 3.9e** shows the SEM micrograph of the Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy which indicates the presence of Al<sub>3</sub>Ni<sub>2</sub> phase (grey contrast), Al<sub>7</sub>Ni<sub>3</sub> phase (intense grey contrast) Al<sub>3</sub>Ta phase (bright contrast), Al<sub>5</sub>Ta<sub>3</sub>Ni<sub>2</sub> phase (intense bright contrast) and (Al)<sub>ss</sub> phase (dark contrast). **Fig. 3.9f** shows the SEM micrograph of the Al<sub>84</sub>Ni<sub>4</sub>Si<sub>12</sub> alloy which indicates the presence of Al<sub>3</sub>Ni phase (bright contrast) and (Al)<sub>ss</sub> phase (dark contrast). It is observed that there are two eutectic reactions takes place i.e., one is a binary eutectic reaction between (Al)<sub>ss</sub> and Al<sub>3</sub>Ni phases.

**Fig. 3.10a** shows the SEM micrograph of the Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloy which indicates the presence of two eutectic reactions with two different morphologies. Two different morphologies are lamellar eutectic structure between (Al)<sub>ss</sub> solid solution phase and Al<sub>2</sub>Cu intermetallic phase and needle type eutectic structure between (Al)<sub>ss</sub> solid solution phase. **Fig. 3.10b** shows the SEM micrograph of the Al<sub>85</sub>Cu<sub>10</sub>Si<sub>5</sub> alloy which indicates the presence of (Al)<sub>ss</sub> solid solution phase with dark contrast and binary and ternary eutectics reactions.

#### **3.4.2.3 Thermal Analysis**

The DSC analysis of the studied alloys was conducted to ascertain the phase transformation temperatures. **Fig. 3.11** shows the DSC thermogram of the studied alloys. It can be observed that all studied alloys with the addition of different alloying elements in Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) ternary alloys as shown in **Fig. 3.11a** and Al-Cu-X (X = Ni and Si) ternary alloys as shown in **Fig. 3.11b** are showing exothermic peaks during the cooling cycle at different temperature values which are very close to the predicted values from CALPHAD

analysis. The DSC curves show the phase transformation for different phases as primary dendritic phase  $\alpha$ -Al and eutectic reactions or formation of intermetallics phases (FCC + Intermetallics) at different temperatures with the different exothermic peaks as shown in **Fig. 3.11**.



**Fig. 3.9:** BSE-SEM micrograph of Al-Ni-X alloys with the effect of (a) Fe (b) Cr (c) Co (d) V (e) Ta and (f) Si.



Fig. 3.10: BSE-SEM micrograph of Al-Cu-X alloys with the effect of (a) Ni (b) Si



**Fig. 3.11:** DSC plots of (a) Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) and (b) Al-Cu-X (X = Ni and Si) alloys.

# **3.4.3** Comparison of phase equilibria using thermodynamic simulation results and experimental results

Thermodynamic simulation suggests the formation of FCC phase, some intermetallics phases (FCC\_A1, BCC\_B2, LAVES phase etc) and binary and ternary eutectic reactions in designed Al-Ni-X and Al-Cu-X ternary alloys as shown in Fig. 3.2 to 3.7. The XRD patterns of the studied multicomponent alloys also showing the existence of FCC phase and a combination of different intermetallics phases as shown in Fig. 3.8. The thermodynamic simulation results can be validated with the help of microstructure analysis of the developed multicomponent alloys. The evolution of different phases during the solidification have been identified with the help of BSE-SEM micrographs attached with EDS analysis. The microstructural analysis also validated the thermodynamic simulation results in a well manner. The DSC analysis of the studied alloys are also confirming the formation of FCC and intermetallic phases at different temperatures that is very close to the predicted values obtained from thermodynamic simulation approach. On the base of these results, it is noteworthy to mention that the thermodynamic simulation using ThermoCalc software is the powerful tool to predict the evolution of different phases during solidification and the solidification behaviour of the studied alloys.

**3.4.4 Mechanical properties of the designed multicomponent alloys** The tensile true stress vs. strain plots of Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) and Al-Cu-X (X = Ni and Si) ternary alloys are shown in **Fig. 3.12. Fig. 3.12a** show the effect of different alloying elements on the mechanical behaviour of Al-Ni-X alloys whereas Fig. 3.12c show the effect of different alloying elements on the mechanical behaviour of Al-Cu-X alloys. The comparison of mechanical properties of studied alloys with the error bars also shown in fig. 3.12b and 3.12d for Al-Ni-X and Al-Cu-X alloys respectively. The mechanical behaviour of the proposed Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) ternary alloys shows the ultimate tensile strength (231.6±8.01 MPa, 193±8.83 MPa, 252.33±6.13 MPa, 256±14.43 MPa, 295.33±8.17 MPa and 200.5±16.12 MPa), yield strength (132.33±6.84 MPa, 115.13±4.32 MPa, 149.67±6.94 MPa, 131.26±6.51 MPa, 137.33±9.56 MPa and 104.47±7.92 MPa) and plastic strain (17.23±2.24%, 11.36±1.15%, 13.83±1.31%, 16.35±1.32%, 18.2±0.75% and 14.87±1.52%) respectively. The mechanical behaviour of the proposed Al-Cu-X (X = Ni and Si) ternary alloy shows the ultimate tensile strength (280 MPa and 235 MPa) and plastic strain (4.29% and 2.1%) respectively. The enhancement in the strength and ductility (234 MPa and 16.7%) for Al-Ni-Fe alloy is because of the existence of bimodal eutectic microstructure. The enhancement in the strength and ductility (259 MPa and 16.5%) for Al-Ni-V alloy is because of the presence of two intermetallics phases and one ternary eutectic phase. The microstructure of Al-Ni-Ta alloy exposes the existence of four distinguish kinds of intermetallics phases. Due to the high-volume fraction of different intermetallics phases, the enhancement in the strength and ductility (296 MPa, 18%) is observed in case of Al-Ni-Ta alloy. The designed Al-Cu-Ni and Al-Cu-Si ternary alloys show the better tensile strength (278±6.16 MPa and 234.3±4.92 MPa), yield strength (140.3±4.1 MPa and 195±3.29 MPa) but with the very high reduction in plastic strain (4.43±0.42% and 2.7±0.58%). The unique microstructure consisting of different intermetallics phases, binary and ternary eutectic reactions provide an opportunity to design novel Albased multicomponent alloys having high strength and plasticity for structural applications.



**Fig. 3.12** True stress vs. strain plots and comparison of mechanical properties of (a, b) Al-Ni-X (X = Fe, Cr, Co, V, Ta and Si) and (c, d) Al-Cu-X (X = Ni and Si) alloys

The effect of different alloying elements on the microhardness of Al-Ni-X and Al-Cu-X ternary alloys is shown in **Fig. 3.13**. **Fig. 3.13a** shows the effect of different alloying elements (Fe, Cr, Co, V, Ta and Si) on the microhardness of the studied Al-Ni alloy system. **Fig. 3.13b** shows the effect of Ni and Si on the microhardness of the studied Al-Cu alloy system. The maximum microhardness which is observed in case of Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy is 284.74  $\pm$ 8 as shown in **Fig. 3.13a**. The most probable reason behind this maximum hardness value is the presence of different hard intermetallics phases like Al<sub>3</sub>Ta and Al<sub>5</sub>Ta<sub>3</sub>Ni<sub>2</sub> phases. **Fig. 3.13b** shows the increment of microhardness value from 147.9 $\pm$ 3.31 HV to 154 $\pm$ 4.83 HV is due to the presence of hard Si phase in case of Al<sub>85</sub>Cu<sub>10</sub>Si5 ternary alloy.



Fig. 3.13 Microhardness variation with the effect of alloying elements on (a) Al-Ni system and (b) Al-Cu system.

#### 3.4.5 Wear behaviour of designed multicomponent alloys

The developed and selected ternary alloys (Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> and Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub>) were investigated through a series of fretting wear test with three different loads, while keeping the number of cycles, frequency, and amplitude remain constant. Fig. 3.14 show the effects of different loading conditions on the fretting wear behaviour of the selected ternary alloys which shows the variation of coefficient of friction (COF) with the number of fretting cycles with the different load conditions at ambient temperature. Fig. 3.14 shows that the values of COF rapidly rise at the beginning of the fretting cycle due to the uneven surface. After a few cycles, a steady state condition develops as the surfaces reach dynamic equilibrium. From Fig. 3.14, it is observed that the fluctuations in the COF values is more in case of normal load of 5N and the fluctuations with COF values continuously decreases with the increment of load from 5 N to 15 N. Due to the debris that accumulates during the test rapidly oxidising, rolling at the interface region, and adhering to the mating surfaces, the COF values fall as the normal load increases. This serves as a protective tribo-layer, preventing direct contact between the specimen and the counter face and therefore reducing the friction. Fig. 3.14a and 3.14b shows the high COF values at 5 N due to the generation of new debris particles and more damage of asperities and with the increment of load from 5 N to 15 N, it's showing the less COF values as compared to the 5 N and this is happening due to the decrease in asperity damage and increment of loads. Fig. 3.14c show the average stable COF values obtained from the fretting wear instrument's data collecting system at the RT tests. It can be observed from the **Fig. 3.14c** that among selected ternary alloys, AlCuNi<sub>1.5</sub> alloy shows lower COF values at all three different loading conditions compare to the AlNiTa<sub>3</sub> alloy. It can be observed that at initially with the increment of load from 5 N to 10 N, a noteworthy decrease in average COF values from 0.96 to 0.76 and from 0.68 to 0.64 for AlNiTa3 and AlCuNi<sub>1.5</sub> alloy respectively. Whereas during the increment of load from 10 N to 15 N, the variation in average COF value is 0.76 to 0.71, 0.64 to 0.62 for AlNiTa3 and AlCuNi<sub>1.5</sub> alloy

respectively. These observations indicate less damage for AlCuNi<sub>1.5</sub> alloy as compared to the AlNiTa<sub>3</sub> alloy.

The wear resistance of the studied ternary alloys with the variation of loads in dry conditions are shown in **Fig. 3.15**. As we know that wear resistance is the inverse of wear rate. It can be observed from **Fig. 3.15** that the  $Al_{93}Ni_4Ta_3$  alloy shows the better wear resistance properties as compare to the  $Al_{88.5}Cu_{10}Ni_{1.5}$  alloys. The specific wear resistance was greatly affected by the increase in hardness values. It is evident from the well-known Archard's principle that the relationship between hardness and wear resistance is one of direct proportionality [153].

The wear scar depth profiles after performing the wear test at different load are shown in **Fig. 3.16**. For Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy, the least depth (30  $\mu$ m) is achieved at 15 N and the maximum depth (40  $\mu$ m) is achieved at 5 N. For Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloy, the least depth (48  $\mu$ m) is achieved at 15 N and the maximum depth (80  $\mu$ m) is achieved at 5 N. **Fig. 3.16** shows that the wear scar depth profiles have a shape that is similar to a "W" or wedge. The 'W' shape indicates that the maximum wear taking place at the centre as compared to the edges. The decrease in the depth indicates the better wear resistance properties.



Fig. 3.14 Coefficient of friction (COF) Vs. Number of cycles at different loads (5 N, 10 N and 15 N) for (a) Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> (b)
Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloy and (c) Comparison of average COF at different loads (d) COF with error bar for both investigated alloys



Fig. 3.15 Wear resistance variation and comparison at different loads



Fig.3.16 Wear scar depth analysis and comparison of studied (a)

Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> (b) Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloys

#### 3.5 Summary

The main findings of this study can be summarized as follows:

 We have successfully designed and developed the multicomponent alloys with the addition of different alloying elements (Fe, Cr, Co, V, Ta and Si) in Al-Ni system and addition of alloying elements Ni and Si in Al-Cu system.

- ii. The developed multicomponent alloys show the (FCC + Intermetallics) microstructures with the formation of different types of intermetallics phases.
- iii. The solidification pathways  $(L \rightarrow L + FCC, L \rightarrow L + intermetallics, L \rightarrow FCC + intermetallics) obtained from ThermoCalc was confirmed and correlated in well manner with the experimental microstructure features.$
- iv. The excellent mechanical properties like tensile strength, microhardness and % elongation of Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> is 296 MPa, 284.74 HV and 18% respectively compare to the other investigated alloys.
- v. The investigated alloys show a noteworthy increase in specific wear resistance with Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy and varying the loads from 5 N to 15 N. The wear resistance of the Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy is 2 times higher as compared to the Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub> alloy and it is 1.5 times higher at 15 N as compared to the load of 5 N.
- vi. The wear scar depth of Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> alloy is 30 μm which is significantly less, indicating better wear properties as compared to the wear scar depth of 48μm in Al<sub>88.5</sub>Cu<sub>10</sub>Ni<sub>1.5</sub>alloy.

#### **3.6 Drawbacks of Al-based low entropy alloys**

The developed multicomponent alloys (Al-based ternary alloys) exhibits microstructure consists of FCC solid solution phase (i.e., Al-rich solid solution phase) and one or more intermetallics. The developed alloys exhibit improvement in strength and ductility, which can be considered as potential candidates for low temperature applications due to thermal stability upto eutectic temperature around (650 °C).

However, the strength can be enhanced further using similar microstructural design consisting of FCC solid solution phase or combination of FCC solid solution phase and one or more intermetallics. Since from the extensive literature review, it is observed that the new metallurgy alloy design concept clearly indicates that the formation of solid solution phase(s) can be achieved using multiple principal elements, which is knows as multicomponent concentrated alloys or popularly known as high entropy alloys (HEAs).

#### 3.7 Importance of High entropy alloys

In recent years, HEAs have attracted the attention of research communities because of their superior mechanical properties and simple solid solution structure. HEAs have emerged as a significant advance in traditional alloy design since 2004, when they were originally proposed independently by Yeh [5] and Cantor [86], and have provided a new path for investigating novel materials with excellent properties. The HEAs show the superior structural properties at room temperatures and elevated temperatures and as a result, these novel HEAs are being investigated as potential candidate materials for a variety of applications, including steam turbines and aerospace sectors. In the past decades, a lot of HEAs have been investigated but it is very difficult to balance the ratio of strength and ductility and therefore, for the balance of strength and ductility, an alloy with a combination of a soft FCC phase and a hard BCC or intermetallic phase could be promising. As an in-situ composite, eutectic structures of the lamellar or rod types have two phases. Furthermore, eutectic materials offer high temperature creep resistance, low-energy phase boundaries, and tunable microstructures.

Therefore, in the current investigation, the main aim is to obtain similar microstructure consisting of FCC solid solution phase(s) or combination of FCC solid solution phase and one or more intermetallics as obtained in multicomponent ternary alloys using similar elements as major principal elements. Hence it is expected to enhance the strength of the designed multicomponent multiprincipal alloys with appreciable ductility and can be taken as a suitable material for high strength and high temperature application.

# Chapter 4

# Design and development of single-phase FCC Fe-Co-Ni-Cr-V-X (X = 0, Al) HEAs

# **4.1 Introduction**

The present chapter explores the design and development of singlephase Fe-Co-Ni-Cr-V-X (X = 0, Al) FCC HEAs by adopting synergistic approach involving thermodynamic simulation, numerical simulation, and experimental techniques. The FeCoNiCr system which leads to multiphase alloy with various refractory element additions was also reported in the literature. We are trying to develop single phase FCC HEA to obtain the required phase equilibria (FCC + Intermetallics). With the help of ThermoCalc software and adding the refractory elements we got the FeCoNiCrV single phase FCC HEA and to develop Al containing single phase HEA, we have added Al in the 5 component HEA and single FCC phase formation confirmed by integrated approach of combining thermodynamic simulation and solidification processing technique.

Among various HEAs,  $Fe_{25}Co_{25}Ni_{25}Cr_{20}V_5$  and  $Fe_{20}Co_{25}Ni_{25}Cr_{20}V_5Al_5$ have been selected for their specific characteristics and properties.

**Fe<sub>25</sub>Co<sub>25</sub>Ni<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>:** This alloy consists of 5 elements, namely iron (Fe), cobalt (Co), nickel (Ni), chromium (Cr), and vanadium (V). The addition of vanadium in this alloy increases its strength and hardness without significantly affecting its ductility. Moreover, the combination of iron, cobalt, and nickel creates a balanced magnetic behaviour, making it suitable for magnetic applications. The presence of chromium provides corrosion resistance, and its high-temperature oxidation resistance is improved by the addition of vanadium.

 $Fe_{20}Co_{25}Ni_{25}Cr_{20}V_5Al_5$ : This alloy consists of the same five elements as Fe25Co25Ni25Cr20V5, but with an additional 5% aluminum (Al). The addition of aluminum enhances its mechanical properties, including strength, ductility, and toughness, making it suitable for applications that require high strength and toughness at elevated temperatures. Additionally, the combination of iron, cobalt, and nickel with chromium and aluminum makes this alloy highly resistant to oxidation and corrosion.

In summary,  $Fe_{25}Co_{25}Ni_{25}Cr_{20}V_5$  and  $Fe_{20}Co_{25}Ni_{25}Cr_{20}V_5Al_5$  were selected for their combination of high strength, hardness, ductility, toughness, magnetic properties, and corrosion resistance. These properties make them suitable for a variety of applications, including aerospace, energy, and manufacturing industries, where highperformance materials are required.

The simulation guided composition was arc melted and verified using structural and microstructural characterization techniques. The present study explores the analysis of solidification behaviour, temperature distribution within the metal casting as well as metal casting to the mould through metal casting-mould interface and phase change during solidification. Two single phase FCC HEAs (Fe-Co-Ni-Cr-V and Fe-Co-Ni-Cr-V-Al) were discussed, and the mechanical properties were compared. The experimental measured hardness of studied single-phase FCC Fe-Co-Ni-Cr-V and Fe-Co-Ni-Cr-V and Fe-Co-Ni-Cr-V-Al HEAs which varies from  $236 \pm 5$  HV to  $272 \pm 4$  HV and  $220 \pm 2.98$  HV to  $259 \pm 5.95$  HV respectively at 500g load is correlated with the simulated cooling curves. The simulated results are in good agreement with the experimental findings. Furthermore, a comparison of the cooling curves of studied HEAs obtained by two simulation techniques is established.

#### 4.2 Objectives

- To design and develop the 5 and 6 components single-phase FCC HEAs with the help of integrated approach of combining thermodynamic simulation, numerical simulation, and solidification processing technique.
- To investigate the phase equilibria study experimentally and compared with the thermodynamic simulation.
- To develop a solidification simulation model to investigate the solidification behaviour of designed single phase FCC HEAs.

• To evaluate the mechanical properties of the designed HEAs and correlated with the numerical simulation results.

#### **4.3 Simulation and Experimental Procedures**

The thermodynamic simulation was done to design the single-phase FCC HEAs and for the analysis of phase formation and temperature variation during the solidification process using the ThermoCalc software version 2021b with the help of TCHEA4 database. The selected HEAs with a nominal composition of Fe<sub>25</sub>Co<sub>25</sub>Ni<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub> and Fe<sub>20</sub>Co<sub>25</sub>Ni<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub> (at. %) were prepared using the vacuum arc melting cum suction casting technique under a protective argon atmosphere using pure metals such as Fe, Co, Cr, Ni, V and Al with a purity level of more than 99.9% and in different shape and size. It is to be noted that Ni was used in the form of square blocks of  $26 \times 26 \text{ mm}^2$  in size, Fe, Cr & Co was used in the form of pieces with irregular shapes, V was used in the form of triangular blocks shape and Al was used in the form of rod having 9 mm diameter. To obtain the homogeneous mixture of all selected elements, the alloy ingot was re-melted five times. After obtaining the casted button-shaped samples, the suction casting was used to produce cylindrical rods with a 6 mm diameter. The structural characterization of the investigated alloy was carried out with the help of XRD analysis operating at 30 mA, 45 KV and step size was  $2\theta = 0.017$  and  $2\theta$  value varied from 20 to 90. Bruker D2 phaser X-ray diffractometer with CuK<sub>a</sub> radiation of  $\lambda = 1.54$  Å was used for this purpose. The microstructure characterization was carried out with the help of FESEM (FESEM model: JEOL, JSM-7610 Fplus) and EBSD analysis. The EBSD technique was used to reveal the phases present in the sample and to understand the microstructure and texture of the HEAs. The sample for EBSD analysis was prepared by following standard metallographic sample preparation techniques, followed by polishing with 0.05µm sized colloidal silica suspension. An area of 1000 μm by 600 μm was scanned at a step size of 1 μm. The sample was kept at a 70-degree tilting condition during the EBSD scan. HKL Channel 5 system and MTEX toolbox in MATLAB software are used for EBSD

data analysis. The solidification simulation was also carried out using the ANSYS Fluent software for suction casting setup and a 6 mm diameter cylindrical cast rod. This program is performed in the system which is operated with 8 GB RAM and an i5 Intel core processor. The hardness value of the developed alloy was measured using a Vickers microhardness tester (Model: MMV-A). The Vickers microhardness was measured at a constant load of 500g with an indentation speed 30  $\mu$ m/s for a dwell time period of 20 seconds. The five different readings were measured at each point across the centre of the sample for the different paths according to the developed simulation model and average hardness value was calculated.

#### 4.4 Results and Discussion

#### 4.4.1 Thermodynamic Simulation

The thermodynamic simulation using the ThermoCalc software is used to predict the possible evolution of the phases during the solidification of the studied Fe-Co-Ni-Cr-V-X (X = 0, Al) HEAs. The thermodynamic simulation results are shown in **fig. 4.1**. **Fig.4.1 (a and a')** showing the amount of phases with the variation of temperature during the solidification process and it is giving the information about the formation of the single FCC phase in the long temperature range from 1700 K to 770 K and 1693 K to 1252 K for 5 and 6 components single phase FCC HEAs, respectively. **Fig.4.1 (b and b')** showing the mole fraction of the solid with the variation of temperature during the whole solidification process. It is also showing the formation of the single FCC phase through a large composition range from liquid to the 0.95 and 0.9 mole fraction of the solid. **Fig. 4.1** confirms the formation of single FCC phase for 5 and 6 components single phase FCC HEAs.



**Fig. 4.1** (a and a') amount of phases vs. Temperature (b and b') *Scheil solidification curve for studied* Fe-Co-Ni-Cr-V-X (X = 0, Al) *single phase FCC HEAs* 

# 4.4.2 Phase Equilibria study of designed single phase FCC HEAs

The evolution of different phases during the solidification has been analysed with the help of XRD FE-SEM attached with EDS and EBSD analysis. The phase transformation temperatures with the evolution of the different phases have been identified with the help of DSC analysis. The detailed analysis of the phase equilibria study is given below:

# 4.4.2.1 Structural characterization

The XRD pattern of the studied single-phase FCC HEAs is shown in **fig. 4.2**. The identification of the peaks confirms the phases which are available in the studied HEAs, and **fig. 4.2 (a and a')** confirm the existence of single FCC phases in the studied Fe-Co-Ni-Cr-V-X (X = 0, Al) single phase FCC HEAs.

# 4.4.2.2 Microstructural characterization

The detailed microstructure characterization of both HEAs is carried out with the help of FESEM as shown in **fig. 4.3 (a and a')**. The microstructure of the studied HEAs shows the presence of a single phase. In order to find the exact phase constitution, the microstructure of the studied HEAs was investigated using EBSD analysis. The phase distribution of the HEAs is shown in **fig.4.3 (b and b')**. EBSD analysis is used to identify the phases which are not possible to detect from XRD due to the present in less % amount (<2%) or if any special orientation is present in the system. So, to get the idea about the phase distribution, EBSD analysis is completed, and it is confirmed that it consists of single phase as shown in **fig. 4.3 (b and b')**.



Fig 4.2 XRD pattern of (a) Fe-Co-Ni-Cr-V (a') Fe-Co-Ni-Cr-V-Al studied single phase FCC HEAs



Fig 4.3 SEM micrograph of (a) Fe-Co-Ni-Cr-V HEA (a') Fe-Co-Ni-Cr-V-Al HEA, Phase distribution map of (b) Fe-Co-Ni-Cr-V HEA (b') Fe-Co-Ni-Cr-V-Al HEA

#### 4.4.2.3 Thermal Analysis

The DSC analysis of the studied single phase HEAs was conducted to ascertain the phase transformation temperatures. **Fig. 4.4** shows the DSC thermogram of the studied HEAs. It can be observed that both studied HEAs are approaching to exothermic peak near to 1400°C which are very close to the predicted values from CALPHAD analysis.



Fig. 4.4: DSC plots of (a)  $Fe_{25}Co_{25}Ni_{25}Cr_{20}V_5$  and (b)  $Fe_{20}Co_{25}Ni_{25}Cr_{20}V_5Al_5$  single phase FCC HEAs.

# 4.4.3 Comparison of phase equilibria using thermodynamic simulation results and experimental results

Thermodynamic simulation suggests the formation of single FCC phase in 5 components Fe-Co-Ni-Cr-V HEA and 6 components Fe-Co-Ni-Cr-V-Al HEA as shown in **fig. 4.1.** The XRD patterns of the studied HEAs also showing the existence of single FCC phase. The thermodynamic simulation results can be validated with the help of microstructure analysis of the developed HEAs. The phase distribution maps for developed HEAs with the help of EBSD analysis are showing the confirmation of single FCC phase. The DSC analysis of the studied HEAs is also confirm the formation of single-phase FCC phase that is very close to the predicted values obtained from thermodynamic simulation approach. On the base of these results, it is noteworthy to mention that the thermodynamic simulation using ThermoCalc software is the powerful tool to predict the evolution of different phases during solidification and the solidification behaviour of the studied alloys.

# 4.4.4 Numerical Simulation

# 4.4.4.1 Solidification Simulation model

It is worthy of mentioning that the current study explores to develop a mathematical model for understanding the solidification process of developed FCC HEAs during vacuum arc melting cum suction casting technique using the ANSYS Fluent software. The split-type copper mould is used during suction casting of HEAs, and the actual half view of split Cu-mould is shown in **fig.4.5 (a)**. The schematic diagram of the selected model is selected based upon the actual dimension of Split Cu-mould, which is taken as 115 mm height (L), 75 mm width (H) and 6 mm diameter (D) of the mould cavity (as shown in **fig.4.5 (b)**). During the casting process, the liquid metal is poured into the mould cavity at a temperature which is greater than the liquid temperature ( $T_L$ ) of the investigated FCC HEAs.





The following assumptions were made during the formulation of the solidification simulation model of single-phase Fe-Co-Ni-Cr-V-X (X = 0, Al) HEAs [56, 60, 154] :

 (i) The heat transfer takes place mainly in conduction mode in the region liquid metal-mould interface to metal mould during the whole solidification process.

- (ii) The heat transfer from the boundary walls of the mould to the environment takes place through the convection mode.
- (iii) The solid mould is homogeneous and uniformly distributed.
- (iv) Pouring is completed without wasting the time and there is no temperature drop during pouring.
- (v) Two-dimensional heat flow was assumed during the phase change procedure.
- (vi) In the metal-mould interface, there are no crest and trough.
- (vii) There is no air gap between metal and mould.

# (a) Grid Independence Study

It is to be noted that the meshing is the most important part of any of the simulation processes. Before starting the simulation process, a grid independence test is essential to select the appropriate mesh size so that there is no effect of the mesh size on the results of the simulation. To conduct the grid independence test, the different temperature values, liquid fraction values are selected for different mesh sizes at three different regions in the metal casting region i.e., at the initial state of the liquid metal pouring in the mould cavity, intermediate location, and final location of the cavity (as shown in **Fig.4.6 (a)**) and solidification time is also calculated for different mesh sizes.

**Fig.4.6** (a) shows the selected points for the testing in the metal casting zone in the mould cavity. The temperature variation w.r.t. mesh size is given in **Fig.4.6** (b) which indicates the temperature variation from 821.27 K to 820.99 K at all three points with the mesh size variation from 2 mm to 0.2 mm which shows almost the same values at all points and temperature is almost constant i.e., 821.03 K after 0.7 mm mesh size. **Fig. 4.6** (b) shows that the perfect mesh size is 0.7 mm. **Fig.4.6** (c) shows that the Liquid fraction w.r.t. mesh size indicating liquid fraction varies from 0.56 to 1 at the mentioned three points with the mesh size variation from 2 mm to 0.2 mm which indicates the same values at all points and shows the constant value of unity after 0.7 mm mesh size. **Fig.4.6** (c) also shows that the perfect mesh size is 0.7 mm. In **fig. 4.6** (b) and (c), it is clear that the temperature values are the same at all the

three points and vary with the mesh sizes and therefore only one line is shown in the figure instead of three lines for three points. Similarly, the solidification time also varies from 0.29 sec to 0.36 sec w.r.t. mesh size with variation from 2 mm to 0.2 mm which shows the constant value of 0.36 sec after 0.7 mm mesh size (as shown in **Fig.4.6 (d)**). From the above grid-independent test results, it is concluded that the perfect mesh size for the solidification simulation is 0.7 mm.



**Fig 4.6** Grid Independence test (a) selected points for the test (b) Temperature Vs. Mesh size (c) Liquid Fraction Vs. mesh size (d) Solidification time Vs. mesh size

#### (b) Time Independence Study

The time step size for each iteration also plays a significant role in performing the simulation. Before starting the simulation process, a time independence test is necessary to confirm the time step size so that there is no effect of the time step on the results of the simulation. To conduct the time independence test, the temperature values at three different regions in the metal casting zone in the mould cavity (as shown in **Fig. 4.6a** i.e., the selected points for the testing in the metal casting zone.) and solidification time for different time steps are selected (as shown in **Fig. 4.7**).

It is observed that the temperature varies from 625 K to 619 K at point 1, 620 K to 614 K at point 2 and 619 K to 613 K at point 3 in the metal casting zone in the mold cavity (as shown in Fig. **4.6** (**a**)). It is to be noted that after 0.001 sec time step size, the temperature is almost

constant i.e., 619 K for point 1, 614 K for point 2 and 613 K for point 3. These constant values are highlighted in the enlarged view of **Fig. 4.7(a)** between 0.002 sec to 0.001 sec.



**Figure 4.7** (a) Temperature Vs. time step size (b) Solidification time Vs. time step size.

**Fig. 4.7(a)** shows the perfect time step size of 0.001 sec. **Fig.4.7(b)** shows that the solidification time varies from 0.36 sec to 0.354 sec, and it is constant (0.354 sec) after 0.003 sec time step size. The constant values are reflected in the enlarged view of **Fig. 4.7(b)** between 0.003 sec to 0.001 sec. From all the above time-independent test results, it is obvious that the perfect time step size for the solidification simulation is 0.001 sec.

# (c) Governing Equation

The governing equations used in the simulation process are given below [155, 156]:

Momentum conservation or Navier-Stokes equation is expressed as

$$\rho \left\{ \frac{\partial \vec{v}}{\partial t} + \nabla \left( \left( \vec{v} \cdot \vec{v} \right) \right) \right\} + \nabla P = \mu \nabla^2 \vec{v}$$
(5.1)

Mass conversation equation is given by

$$\nabla . \vec{v} = 0 \tag{5.2}$$

Energy conservation equation can be written as follows:

$$\partial/\partial t (\rho H) + \nabla (\rho \vec{v} H) = \nabla (k \nabla T)$$
 (5.3)

Where P, H,  $\rho$ ,  $\mu$  and  $\vec{v}$  are the representation of pressure, enthalpy, density, viscosity of the fluid and velocity, respectively.

For the above-said solidification simulation process, an enthalpy porosity method is used. This method is used to track the phase change interface with the help of the mushy region[155, 157]. The advantage of this method is that it is easy to use a mushy region instead of a single point to track the temperature change during the solidification. This mushy region is called a pseudo zone which is a porous zone, and the porosity of the zone is calculated with the help of one parameter which is known as a liquid fraction. The value of the liquid fraction is calculated based on the enthalpy balance at each cell in each iteration. The liquid fraction value varies from 0 to 1. The liquid fraction of the fully solid region is 0 and for the fully liquid region, the liquid fraction is taken as 1. Using the enthalpy porosity method [154, 155], enthalpy is calculated with the help of an energy equation as given in equation 5.3, Where enthalpy H is given by

$$H = h + \Delta H \tag{5.4}$$

Equation 5.4 signifies the sum of two terms in which the first term is represented by sensible heat and the other term is known as latent heat.

The sensible heat is calculated as given below:

$$h = \mathbf{h}_0 + \int_{To}^T Cp \ dT \tag{5.5}$$

Where  $h_0$  is the reference enthalpy,  $T_0$  is the reference temperature,  $C_p$  is the specific heat at constant pressure and T is the temperature at which the enthalpy will be calculated.

The latent heat is calculated using an equation as given below:

$$\Delta H = \beta L \tag{5.6}$$

Where  $\beta$  is known as the liquid fraction which can be defined as

$$\beta = \begin{cases} 1 & \text{if } T > T_{\text{liquidus}} \\ (T - T_{\text{solidus}}) / (T_{\text{liquidus}} - T_{\text{solidus}}) & \text{if } T_{\text{solidus}} < T < T_{\text{liquidus}} \\ 0 & \text{if } T < T_{\text{solidus}} \end{cases}$$
(5.7)

In equation 5.7, T is the representation of temperature value in the mushy region;  $T_{liquidus}$  &  $T_{solidus}$  are the two temperature limits of the solidification range. As the solidification process lies between  $T_{liquidus}$  &  $T_{solidus}$ .

Equations 5.6 & 5.7 denote that the latent heat of the metal casting can change from 1 (for liquid state) to 0 (for solid-state). The evaluation of the temperature during the solidification is an iterative procedure between equation 5.3 and equation 5.7.

#### (d) Initial conditions & boundary conditions

At the initial stage, the temperature of the molten metal which was poured in the mould cavity was taken as 1750 K (54 K superheat than the liquidus temperature of the studied HEA) in case of Fe-Co-Ni-Cr-V HEA and 1730 K (50 K superheat than the melting point of the alloy) in case of Fe-Co-Ni-Cr-V-Al HEA and the temperature in the copper mould was taken as 300 K. The initial temperature of the air was fixed at 300 K. For the selected computational domain, boundary conditions were the heat transfer mode from the mould to the environment was selected as convection heat transfer and the heat transfer coefficient between the mould and the environment was 10 W /  $m^2$ K.

# (e) Thermophysical Properties

The thermophysical properties of the selected HEAs (casting metals) and the copper mould are given in **table 4.1**.

# 4.4.4.2 Contours of liquid fraction during the solidification

In the suction casting process of the selected single-phase HEAs, the contours of the liquid fraction at a different time instant during the solidification process are shown in **fig.4.8**. At the initial stage (0 sec), the molten metal at or above liquidus temperature is filled in the mould cavity, which is completely in the liquid state i.e., liquid fraction ( $\beta$ ) = 1. Just after the pouring of the molten metal, heat transfer takes place from the metal cast zone to the mould zone and the liquid fraction value continues to decrease (as shown in **fig. 4.8**). At 0.23 sec and 0.27 sec, the solidification is completed and the whole liquid is transformed to the solid phase for 5 and 6 components single phase HEAs, respectively.

Therefore, liquid fraction value is considered as 0 at 0.23 sec and 0.27 sec for 5 and 6 components single phase HEAs respectively, indicating the completely solid state which is described earlier using the enthalpy porosity method. The most important time instant is 0.22 sec and 0.26 sec for 5 and 6 components single phase HEAs respectively because it is the last time instant when the metal is in a liquid state which means this region will solidify at the last moment of the solidification. At 0.22 sec and 0.26 sec, the liquid region shows the last solidification zone or hotspot region during the solidification. This hotspot region is in the centre of the cylindrical casting. So, it is found that the solidification time for the investigated alloys (Fe-Co-Ni-Cr-V and Fe-Co-Ni-Cr-V-Al HEAs) is 0.23 sec and 0.27 sec respectively for the suction casting process. The identification of the hotspot region will help to improve the solidification time for a casting. By changing the pouring location or system, the solidification time and properties of the alloy can be improved.

Properties	Value		
	Fe-Co-Ni-Cr-V	Fe-Co-Ni-Cr-V-Al	Mould
Thermal	88.14 W / m-K	72.285 W/m-K	401 W/m-
Conductivity			К
Specific Heat	446.5 J / Kg-K	469.55 J/Kg-K	390 J/Kg-
Capacity			К
Density	7671 Kg / m <sup>3</sup>	7695.4 Kg/m <sup>3</sup>	8940
			Kg/m <sup>3</sup>
Latent Heat	304950 J / Kg	312400 J/Kg	-
Viscosity	0.004905 Kg /	0.004695 Kg/m-K	-
	m-K		
Liquidus	1696 K	1680 K	-
Temperature			
Solidus	1628 K	1642 K	-
Temperature			

 

 Table 4.1: Thermophysical properties of both casting metals and mould



Figure 4.8 Contour of liquid fraction at (a) 0 sec (b) 0.05 sec (c) 0.1 Sec (d) 0.2 sec (e) 0.22 sec (f) 0.23 sec for Fe-Co-Cr-Ni-V HEA and (a') 0 sec (b') 0.05 sec (c') 0.1 Sec (d') 0.2 sec (e') 0.26 sec (f') 0.27 sec for Fe-Co-Cr-Ni-V-Al HEA

# **4.4.4.3** Temperature profiles of casting metal during the solidification

The temperature distribution within the metal cast zone is shown in **fig. 4.9**. The Colour gradient in the profiles shows the distribution of the temperature across the liquid metal at a particular time. At the initial stage, the temperature of the metal is 1750 K and 1730 K for both alloys which is shown in red colour. After some time, heat transfer takes place from metal casting to the mould and then mould to the environment. The obtained temperature profiles indicate that the temperature starts to decrease from the surrounding of the mould after contact with the mould which is at room temperature. **Fig. 4.9** shows the continuous decrease of the temperature during the liquid to solid phase transformation of the studied HEAs.

# 4.4.4 Temperature profiles of mould during the solidification

The corresponding temperature profiles for the mould are shown in **fig. 4.10**. At the initial stage, the mould is at 300 K and after that heat transfer from the metal casting to mould takes place and the temperature continues to increase. These profiles signify the increment of the temperature from the inner side to the outer side, revealing the heat transfer from the metal casting to the mould.



Figure 4.9 (A & B) Contour of temperature of cast metal at (a) 0 sec (b) 0.05 sec (c) 0.1 Sec (d) 0.2 sec (e) 0.22 sec (f) 0.23 sec for Fe-Co-Cr-Ni-V HEA and (a') 0 sec (b') 0.05 sec (c') 0.1 Sec (d') 0.2 sec (e') 0.26 sec (f') 0.27 sec for Fe-Co-Cr-Ni-V-Al HEA



Figure 4.10 (A & B) Contour of temperature of mould at (a) 0 sec (b) 0.05 sec (c) 0.1 Sec (d) 0.2 sec (e) 0.22 sec (f) 0.23 sec for Fe-Co-Cr-Ni-V HEA and (a') 0 sec (b') 0.05 sec (c') 0.1 Sec (d') 0.2 sec (e') 0.26 sec (f') 0.27 sec for Fe-Co-Cr-Ni-V-Al HEA

# 4.4.4.5 Cooling curves during the solidification

The plots between temperature and time for the studied single-phase FCC HEAs are shown in **fig.4.11& 4.12**. Different paths are shown in the vertical direction from path 1 to path 11 and in each path, there are 7 points in the longitudinal direction with the distance of 1 mm (as shown in **fig. 4.11 (a)**). **Fig. 4.11** shows the cooling curves for the
different paths (Path 3, Path 5, Path 7, and Path 9 as shown in **fig. 4.11** (a)) across the metal casting zone for the selected points (a to g). It is observed that all four curves show the behaviour of heat transfer from the metal cast to the mould. The most important thing is that the centre points show different behaviour than other points and found that the cooling effect is faster from the centre to the metal-mould interface. As it is seen from the figure that the centre point 'd' shows the slow cooling effect as compared to the fast cooling at point 'a & g'. It is to be noted that the symmetric heat transfer is observed for all the selected paths from the centre to the metal-mould interface. Due to the symmetric heat transfer, the temperature variation is same for points 'a & g', 'b & f' and 'c & e' and the curve are overlapping to each other due to the same temperature value. Therefore, **Fig. 4.11** show the 4 lines instead of 7 lines for the 7 points.



Fig. 4.11 (a) Selected points across the longitudinal direction and 11 paths along the vertical direction of the sample, Cooling curve across the sample in the longitudinal direction for (b, b') Path 3 (c, c') Path 5 (d, d') Path 7 (e, e') Path 9 for both investigated alloys

**Fig. 4.12 (a)** shows the selected points across the metal cast zone vertically and horizontally to characterize the cooling behaviour of the studied single-phase FCC HEAs and **fig. 4.12 (b and b')** shows the cooling behaviour of the given HEAs for the selected 21 points up to 1 sec and 1.5 sec for 5 and 6 components single phase FCC HEAs, respectively. At point 8 to 14, the phase change is observed within the range of 1695 K to 1630 K and 1686 K to 1583 K for 5 and 6 components single phase FCC HEAs, respectively. At the other points, the phase changes curvature was not observed due to fast cooling. This curve also shows the same behaviour at the centre and the metal mould interface. The centre points (8 to 14) show the slow cooling behaviour as compared to the other points (1 to 7 & 15 to 21).



**Fig. 4.12** (a) Selected points in the specimen (b) Cooling curve for the selected points up to 1 sec for Fe-Co-Ni-Cr-V HEA (b') Cooling curve

for the selected points up to 1 sec for Fe-Co-Ni-Cr-V-Al HEA

## **4.4.6 Heating and cooling curve of the mould during the solidification**

The heat transfer analysis is also carried out in the mould. To study the heat transfer phenomenon, 24 points are selected in the mould as shown in **fig.4.13** (**a**). At these points, the temperature values are obtained at different time instant during the solidification. **Fig. 4.13** (**b** and **b**') shows the heating and cooling curve for the mould during the heat transfer from the metal cast to the mould. Points 1 to 4 and 13 to 16 show the heating and cooling behaviour because these points are selected near to the metal cast zone in the mould cavity. For the other points, there are only heating behaviour because these points are far from the metal cast zone. It is seen from the **Fig. 4.13** (**b** and **b'**) that as the distance increases from the cast metal, the raising of the temperature is very slow.



Fig. 4.13 (a) Selected 24 points in the mould; Heating and cooling curve for the selected points up to (b) 1 sec for Fe-Co-Ni-Cr-V HEA (b') to 1.5 sec for Fe-Co-Ni-Cr-V-Al HEA

## 4.4.5 Mechanical properties of the designed single-phase FCC

## HEAs

The tensile true stress vs. strain plots of 5 and 6 component single phase FCC HEAs (Fe-Co-Ni-Cr-V and Fe-Co-Ni-Cr-V-Al) are shown in Fig. 4.14. The tensile strength and plastic strain of 5 component Fe25Ni25Co25Cr20V5 and 6 component Fe20Ni25Co25Cr20V5Al5 single phase FCC HEAs are (485 MPa, 54.3%) and (518 MPa, 64.84%) respectively. Fig. 4.14 6 shows that the component Fe20Ni25Co25Cr20V5Al5 single phase FCC HEA show the better mechanical properties compare to the 5 component Fe<sub>25</sub>Ni<sub>25</sub>Co<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub> single phase FCC HEA. Therefore, 6 component single phase HEA is the potential candidate to analysis of hot deformation behaviour and check the possibility for high strength and high temperature applications.



**Fig. 4.14** (a) Tensile Stress-Strain curve (b) Comparison of UTS, YS and % Elongation with error bar for 5 and 6 component single phase FCC HEAs

# 4.4.6 Correlation of the mechanical properties between the Experimental and numerical approaches

Khiyon et. al [158] reported that when the cooling rate is high, the grain size will reduce and hence increases the hardness of the alloy. Sahoo et. al [59] reported a relationship between hardness and solidification growth velocity or cooling rate as below:

$$H_v = \mathbf{K}^* V^{\mathrm{m}} \tag{4.8}$$

Where  $H_v$  is the Vickers hardness value, V is the solidification growth velocity, m is the exponent value and K is the constant.

From equation (4.8), it is obvious that higher the solidification growth velocity or cooling rate leads to the higher hardness and vice versa.

Earlier it is described the cooling curve at different points and paths along with the sample and across the sample. For validation of the simulation work, the two paths 3 & 7 and the points across the sample are selected which are located at the centre and both side of the centre at 1 mm distance each (as shown in **fig.4.15** (**a**)). The cooling curve at path 3 and path 7 are shown in fig.4.15 (c and c') & (d and d'). It is clear from the figure that, the cooling rate at the centre is slow and increase from the centre to outer side in a symmetric way. Due to the symmetry from the centre to outer side, the temperature at point 2 & 4 and 1 & 5 are same. The actual view of the as-cast studied HEAs sample with the presentation of path 3 & path 7 (as shown in fig.4.16 (a and a')). The cooling rate is obtained from the cooling curve at the first instant of the solidification at different points from the centre as well as at the centre which is shown in fig.4.16 (b and b') & (c and c'). The microhardness at different points and paths are measured using the micro-Vickers hardness tester (as shown in fig.4.16 (d and d') & (e and e')).

From the **fig.4.16**, it is seen that the cooling rate behaviour obtained from the simulation is matched with the experimental measured hardness. At the centre of the mould cavity, the cooling rate is slow and hence the hardness is less as compared to the other points away from the centre. The hardness varies from  $\approx 236 \pm 5$  to  $260 \pm 4$  HV and  $224.71 \pm 3.29$ HV to  $258.73 \pm 5.95$  for path 3 (as shown in **fig. 4.16 (d and d')**) and for path 7, the hardness varies from  $\approx 239 \pm 3$  to  $272 \pm 4$  HV and  $219.67 \pm 2.98$  HV to  $251.2 \pm 5.08$  HV (as shown in **fig. 4.16 (e and e')**). From the centre to the outer side of the sample, the cooling rate increases and hence hardness also increases. This phenomenon gives the validation of the simulation work during solidification of single-phase HEAs using the vacuum arc melting cum suction casting solidification technique.



**Fig. 4.15.** Validation of the simulation result (a) heat transfer profiles obtained using ANSYS Fluent software showing path 3 and path 7 (b and b') cooling curve for path 3 (c and c') cooling curve for path 7 for

5 and 6 components single phase HEAs respectively

## 4.4.7 Comparison of numerical simulation results with thermodynamic simulation results

ThermoCalc simulation was carried out to validate the solidification process for single-phase FCC HEAs with solidification simulation work using ANSYS Fluent software. ThermoCalc software [159] is used to predict the solidification path during the solidification from liquid to solid transformation [12]. The Scheil solidification curve which is obtained from the ThermoCalc software is shown in **fig. 4.17 (a and a')**. It is showing the variation of temperature with the variation of fraction of solid. The temperature variation with the variation of fraction of solid during solidification process is noted with the help of ANSYS Fluent software. The temperature w.r.t fraction of solid curve is shown in **fig. 4.17 (b and b')**. During the solidification process, fraction of the solid changes from 0 to 1. At a particular value of the solid fraction, temperature value is obtained with the help of ThermoCalc software and

ANSYS Fluent software (as shown in **fig. 4.17 (b and b')**). The two solidification simulation results obtained using ThermoCalc software and ANSYS Fluent software was compared (as shown in **fig. 4.17 (b and b')**). From the **fig.4.17 (c and c')**, it is found that there is only 1.22 % and 2.41% error which is under the acceptable value or lower than that obtained by other researchers for simulation validation [160] and R value is 0.772 and 0.637 which signifies the good correlation between ANSYS Fluent simulation results and ThermoCalc simulation results. With the help of **fig.4.17 (c and c')**, it is stated that ANSYS Fluent software can also be possible to predict the solidification process. Therefore, the solidification simulation results using ANSYS Fluent software is with good agreement and acceptable with the ThermoCalc simulation result.



**Fig 4.16** Validation of the simulation result (a and a') As cast sample (b and b') cooling rate for path 3 (c and c') cooling rate for path 7 (d and d') Micro Hardness at different points for path 3 (e and e') Micro Hardness at different points for path 7 for 5 and 6 components single

phase FCC HEAs respectively



Fig. 4.17 (a, a') Scheil solidification curve from ThermoCalc software(b, b') Comparison of solidification simulation results obtained usingANSYS Fluent software and the ThermoCalc software. (c, c')

Pearson's coefficient and AARE value for the ANSYS Fluent simulation for 5 and 6 components single phase HEAs respectively

## 4.5 Summary

The multicomponent FeCoNiCrV-X (X = 0, Al) single phase FCC HEAs are successfully synthesized using the vacuum arc melting unit followed by suction casting setup. The solidification behaviour of the studied alloy has been completed with the help of ANSYS Fluent software. On the base of the detailed analysis and the discussions, summary of the study is given below:

- I. The studied HEAs is showing the formation of FCC single phase which will be helpful to create the new phase equilibria according to the requirement.
- II. A solidification simulation model for single-phase FCC HEAs is developed using the ANSYS Fluent software which provides the

complete visualization of the solidification using vacuum arc melting cum suction casting technique.

- III. The simulated results provide the temperature history at different time instant of solidification for metal casting and mould, liquid fraction profiles during the solidification.
- IV. The liquid fraction simulated results signify the cooling rate varying from 550 K/sec to 3500 K/sec for path 3 and 580 K/sec to 4080 K/sec for path 7. It is found that the solidification takes place at faster rate within 0.23 sec and 0.27 sec due to high cooling rate and the last hotspot region at 0.22 sec and 0.26 sec for 5 and 6 components single phase HEAs, respectively.
- V. The hardness varies from  $\approx 236 \pm 5$  to  $260 \pm 4$  HV and  $224.71 \pm 3.29$  HV to  $258.73 \pm 5.95$  for path 3 and for path 7, it varies from  $\approx 239 \pm 3$  to  $272 \pm 4$  HV and  $219.67 \pm 2.98$  HV to  $251.2 \pm 5.08$  HV for 5 and 6 components single phase HEAs, respectively. The experimental measured hardness is in good agreement with the simulated cooling rate behaviour.
- VI. The solidification simulation results obtained using two simulation software are in good agreement within 1.22 % and 2.44% error for 5 and 6 components single phase HEAs, respectively.
- VII. The comparison between solidification simulation by numerical approach and thermodynamic simulation method with reasonable accuracy has been established and subsequently the cooling rates obtained by simulation approach with experimental measured hardness is successfully validated.
- VIII. The 6-component single phase FCC HEA show the better mechanical properties (518 MPa, 64.84%) compare to the 5component single phase FCC HEA and it is selected for further thermomechanical processing work for high strength and high temperature applications.

## Chapter 5

## Hot deformation behaviour of 6 components FeCoCrNiVAl single phase FCC HEAs

### **5.1 Introduction**

The hot deformation behaviour of the studied  $Fe_{20}Co_{25}Ni_{25}Cr_{20}V_5Al_5$ single phase FCC HEA is investigated in the temperature range from 1073 K to 1323 K at the different strain rate range from  $10^{-3} s^{-1}$  to  $1 s^{-1}$ . On the base of the detailed analysis of the processing maps and microstructural phenomena of the deformed samples, the optimum conditions for the further working conditions are 1173 K to 1323 K and strain rate ranges are  $10^{-1} s^{-1}$  to  $1 s^{-1}$ . The deformation behaviour is explained using EBSD analysis and correlated with the dislocation movement and grain boundaries distribution. The hot deformation behaviour of the multicomponent Fe-Co-Ni-Cr-V-Al single-phase FCC HEA is predicted by using constitutive models or mathematical modelling. The prediction of flow stress using ANN modelling shows the best agreement with the experimental measuring among all modelings having less than 4% error.

## **5.2 Experimental Procedure**

Isothermal hot compression test was performed using the Gleeble@3800 thermo-mechanical simulator to understand the hot deformation behaviour of studied single-phase FCC HEA at a higher temperature and different strain rates. The specimen used for the hot compression testing is in rod shaped having 6 mm diameter and an aspect ratio of 1.5:1. The isothermal compression test were performed at the different temperature as 800°C (1073 K), 900°C (1173 K), 1000°C (1273 K) and 1050°C (1323 K) with the different strain rate as  $10^{-3}$  s<sup>-1</sup> (0.001),  $10^{-2}$  s<sup>-1</sup> (0.01),  $10^{-1}$  s<sup>-1</sup> (0.1) and 1 s<sup>-1</sup> (1). To minimize the friction between sample ends and anvil, a graphite sheet along with Ni paste is used which provide the sufficient lubrication during the hot deformation test. Before starting the hot compression test, the specimen was heated

at a 5 K/s heating rate from the room temperature to the required testing temperature and after that 5 min soaking time is given to each sample at the same temperature for homogenous distribution of the temperature throughout the sample. The whole compression test was performed in an inert atmosphere by using the argon gas. The all samples were subjected to true strain of 0.65 that is equal to 50% reduction in the sample height and after that all samples were water quenched to the room temperature and freeze the hot deformed microstructure. During the whole hot compression process, the true stress- strain detail was recorded for all deformation temperatures and strain rates. The analysis of the microstructure evolution and compositional analysis of deformed samples of studied HEA were studied by the SEM attached with the EDS. The microstructure of the deformed samples was carried out along the compression axis.

## 5.3 Results and Discussion

## 5.3.1 Mechanical behaviour of the single-phase FCC HEA

True Stress-strain curves of the single-phase HEA were obtained at different temperatures (1073 K, 1173 K, 1273 K, 1323 K) and different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup>, 1 s<sup>-1</sup>) during the hot deformation testing process as shown in **fig 5.1.** The suction casted sample was used for the testing which is in the cylindrical shape of 6 mm diameter with an aspect ratio of 1.5:1.

### 5.3.1.1 Flow behaviour of single-phase FeCoCrNiVAl FCC HEA

Fig. 5.1 (a) to (e) show the relationship between true stress ( $\sigma$ ) and true strain ( $\epsilon$ ) of the multicomponent FCC single phase FeCoCrNiVAl HEA. It is observed from the fig. 5.1 (a) to (d) that the stress is decreasing with the increase in the temperature at a constant strain rate and it is increasing with the increase in the strain rate at a particular deformation temperature. As we know that the two mechanisms named as strain hardening and softening plays a very important role during the hot deformation analysis. At the initial stage, flow Stress is increasing the maximum stress value, the dislocation generation rate is increases

rapidly so that the strain hardening phenomena is in a dominant stage. Due to the rise in dislocation density with the increase of strain, flow stress is increasing and reached at the maximum level. After the peak stress, softening process plays the dominant role and the flow stress is falls or almost constant as shown in **fig. 5.1**.



**Fig 5.1** True stress-strain curve for the studied single-phase HEA at different strain rates (a)  $\dot{\varepsilon} = 1 S^{-1} (b) \dot{\varepsilon} = 0.1 S^{-1} (c) \dot{\varepsilon} = 0.01 S^{-1} (d) \dot{\varepsilon} = 0.001 S^{-1} (e) \log (\dot{\varepsilon})$  Vs. Temperature

## 5.3.1.2 Deformation behaviour of single-phase FeCoCrNiVAl FCC HEA using EBSD analysis

The EBSD microstructures of all samples after deformation at different temperature and strain rate are shown in **Fig. 5.2**. It has to be noted that

no cleaning was applied during the analysis. It is observed that the microstructure evolution is different at different strain rates and temperatures. This difference in microstructure evolution at different combination of temperature and strain rate indicates that the relative activity of different slip systems are different during deformation.



Fig. 5.2 Inverse pole figure (IPF) maps at (a to d) 1073 K (e to h) 1173
K (i to l) 1273 K (m to p) 1323 K with different strain rate such as 0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup> and 1 s<sup>-1</sup> respectively.

Samples deformed at 800°C (1073 K) do not show the presence of small grains in the microstructure. However, the presence of small grains decorating the parent grain bounday is observed at  $0.001s^{-1}$  at 1173 K,  $0.001s^{-1}$  to  $0.01s^{-1}$  at 1273 K, and  $0.001s^{-1}$  to  $0.1s^{-1}$  at 1323 K. Further, the presence of deformation bands is observed in large grains of all samples and one such grain for the sample deformed at  $0.001s^{-1}$  at 1073 K is shown in **Fig. 5.3** (marked with grain number '1' and '2' in **Fig. 5.3**).



**Fig 5.3** Deformation bands in large grains of the deformed sample at 800°C (1073 K) and 0.001 s<sup>-1</sup>

The presence of deformation bands in the present alloy suggests that the stacking fault energy of the material is low and slip is channeled in the grain through the deformation bands. As the deformation temperature is increased, small grains appeared in the boundaries of large grains. The presence of small grains is observed at strain rate of 0.001 s<sup>-1</sup> and 0.01s<sup>-1</sup> at 1000°C. The small grains are partitioned from the rest of the microstructure and are analyzed for two of the samples deformed at 0.001s<sup>-1</sup> and 0.01 s<sup>-1</sup> at 1000°C (see **Fig. 5.4**) though similar observation is noticed at other combinations of temperature and strain rate.

Deformation bands are formed during low temperature deformation of the sample. But when the same material is deformed at high temperature, small grains pop out at the grain boundaries. Hence, to understand the orientation of small grains, the microstructure is partitioned from the parent grains in the Fig. 5.4. Finally, the texture of the deformed and small grains is calculated and compared in the Fig. 5.4. It is observed that there is no difference in the texture between the parent and small grains.



**Fig.5.4** Small and large grain distribution profiles for (a to c) 1000°C and 0.001s<sup>-1</sup> & (d to f) 1000°C and 0.01s<sup>-1</sup>

It is observed that the orientation of small grains are same that of large grains indicating that small grains are produced from large grains by the gradual conversion of low angle grain boundary of 2-5° to 15-180° type. To confirm it, the EBSD microstructure superimposed with grain boundaries is shown in **Fig. 5.5** for samples deformed at 1000°C, 0.001s<sup>-1</sup> showing the presence of low angle grain boundaries adjacent to the high angle grain boundaries suggesting the gradual conversion of low angle boundaries to high angle boundaries. This gradual conversion of grain boundaries at high teperature under loading is an indication of continus dynamic recovery and recrystallization mechanism.



Fig. 5.5 (a) Inverse pole figure (IPF) maps at 1000°C, 0.001s<sup>-1</sup> (b)
Magnified regions of the circle (marked in Fig. 6.5a) showing the presence of LAGBs and HAGBs

## **5.3.1.3** Correlation between mechanical behaviour with the dislocations of single-phase FeCoCrNiVAl FCC HEA

The true stress versus true strain curve indicates that stress value decreases with increase in temperature as well as decrease in strain rate during deformation. The increase or decrease in stress value is related to the dislocation content in the material which is generated during deformation. Hence, to compare the dislocation of different samples, hardening plot was plotted for all samples and is shown in **Fig. 5.6**.

The hardening curves show a decrease in the value of hardening rate with increase in the stress value at all temperatures. At 0.001s<sup>-1</sup>, the hardening rate decreases with increase in temperature till 1000°C but at 1050°C, the value of hardening rate is higher than 1000°C. The decrease in the rate of hardening till 1000°C can be attributed to the conversion of dislocations to low angle grain boundaries (LAGBs) which finally converted into high angle grain boundaries (HAGBs).



**Fig.5.6** Rate of hardening Vs. True Stress plots at different strain rates (a)  $0.001 \text{ s}^{-1}$  (b)  $0.01 \text{ s}^{-1}$  (c)  $0.1 \text{ s}^{-1}$  and (d)  $1 \text{ s}^{-1}$ 

The higher rate of hardening at 1050°C compared to 1000°C can be attributed to the presence of high volume fraction of  $\Sigma 3$  boundaries which are stable in nature and refined the microstructure significantly resulting in enhancing the cross slip of dislocaions. The microstructural analysis shows that nearly 43%  $\Sigma$ 3 (see Fig. 5.7) boundaries are present in the sample after deformation. The sample deformed at a strain rate of 0.01s<sup>-1</sup> shows the increase in hardening rate till 900°C. However, once sub-grain formation starts i.e at 1000°C, hardening rate decreases because new grains are produced by the gradual conversion of LAGBs to HAGBs which is consistent with the sample deformed at 0.001s<sup>-1</sup> at 900°C and 1000°C. As the deformation temperature increases, more number fraction of LAGBs converted to HAGBs resulting in the decrease in the rate of hardening values with increase in the temperature. The sample deformed at strain rate of  $0.1s^{-1}$  in the temperature range of 800°C to 1050°C is not showing any trend in the hardening behavior which can be attributed to the heterogeneous strain distribution during deformation compared to the sample deformed at lower strain rate leading to the highest hardening rate at 1050°C. The sample deformed at a strain rate of 1s<sup>-1</sup> shows overall increase in hardening rate with increase in temperature which is attributed to the increase in the cross

slip of dislocation with increase in temperature. Further, high strain rate of deformation leads to the heterogeneous strain distribution in the microstructure compared to the sample deformed at low strain rate.



**Fig. 5.7** Microstructure analysis with the grain boundaries distribution after deformation at 1050°C temperature and 0.001 s<sup>-1</sup> strain rate.

## **5.3.2.** Optimization of deformation conditions and processing maps of the single-phase FCC HEA

The processing map can provide the information about the optimum deformation condition and to describe the flow instability domains. Thus, the processing maps give the strategy about secondary processing windows towards safe side of temperature and strain rate which is based on the instability parameters and power dissipation efficiency [161]. Therefore, in the present study, the processing maps of the Fe-Co-Cr-Ni-V-Al single-phase HEA are generated using the dynamic material modelling (DMM) using the combination of power dissipation efficiency ( $\eta$ ) and instability parameter  $\xi$  ( $\dot{\epsilon}$ ) contour maps. The assumptions of this model during the hot working process are that the plastic flow is nonlinear, dynamic, and irreversible [162, 163]. The total energy absorbed during the hot deformation process is defined by the multiplication of flow stress and strain rate and it is given by the equation

$$\mathbf{P} = \boldsymbol{\sigma}.\dot{\boldsymbol{\varepsilon}} = \int_0^{\dot{\boldsymbol{\varepsilon}}} \boldsymbol{\sigma} . d\dot{\boldsymbol{\varepsilon}} + \int_0^{\boldsymbol{\sigma}} \dot{\boldsymbol{\varepsilon}} . d\boldsymbol{\sigma}$$
(5.1)

The total energy absorbed during the process can be divided into two parts as reported by Prasad et. al. [164] and it is given by the sum of  $E_P$ and  $E_M$  where  $E_P$  is defined as the energy which is dissipated during the plastic deformation and  $E_M$  is defined as the energy which is dissipated during the microstructure changes through metallurgical process such as phase transformation, dynamic recrystallization and dynamic recovery, internal fracture etc during the hot deformation process. So, the equation 1 can be rewritten as given below:

$$P = \sigma.\dot{\varepsilon} = \int_0^{\dot{\varepsilon}} \sigma.d\dot{\varepsilon} + \int_0^{\sigma} \dot{\varepsilon}.d\sigma = E_P + E_M$$
(5.2)

In DMM Model, the strain rate sensitivity, power dissipation efficiency and instability parameter are the key parameters.

### **5.3.2.1** Strain rate sensitivity parameter (m)

Strain rate sensitivity parameter is one of the most essential parameters for the hot deformation mechanism of materials and hot workability is also affected by this parameter. According to the Prasad et. al. [164] Strain rate sensitivity parameter is calculated by the derivative of stress w.r.t. strain rate or partial derivative of  $\log \sigma$  w.r.t.  $\log \dot{\varepsilon}$  at constant strain ( $\varepsilon$ ) and working temperature (T). Strain rate sensitivity parameter (m) is given by the expression as shown below:

$$\mathbf{m} = \frac{d\sigma}{d\dot{\varepsilon}} = \left(\frac{\partial \ln\sigma}{\partial \ln\dot{\varepsilon}}\right)_{\mathrm{T},\,\varepsilon} \tag{5.3}$$

Where  $\sigma$  is represented by effective flow stress,  $\dot{\varepsilon}$  is represented by strain rate, T is represented by working temperature and  $\varepsilon$  is represented by strain.

## 5.3.2.2 Power dissipation efficiency $(\eta)$

Power dissipation efficiency is also a key parameter for DMM modelling. The power dissipation during metallurgical process is calculated by the given equation

$$E_{\rm M} = \int_0^\sigma \dot{\varepsilon} \cdot d\sigma = \frac{\sigma \cdot \dot{\varepsilon} \cdot m}{m+1}$$
(5.4)

With the help of equation 5.4, we can calculate the power dissipation at the given temperature and strain rate sensitivity parameter. The maximum value of the  $E_M$  is obtained when m is equal to 1 under the linear power dissipation condition and thus the maximum of  $E_M$  is given by

$$E_{M_{max}} = \frac{\sigma \cdot \dot{\varepsilon}}{2} \tag{5.5}$$

If the power dissipation capacity of the material is expressed in terms of power dissipation efficiency, then we can easily visualize the effect of  $E_M$  on the plastic flow of the material. Therefore, the power dissipation efficiency is defined as the ratio of  $E_M$  to the  $E_{M_{max}}$  and it is given by the expression as shown below

$$\eta = \frac{E_M}{E_{M_{max}}} = \frac{2m}{m+1} \tag{5.6}$$

The nonlinear power dissipation conditions are used to plot the contour maps of power dissipation efficiency using the equation 5.6 which refers the variation of efficiency with the temperature and strain rate.

## 5.3.2.3 Instability Parameter (ξ (έ))

To identify the stable and unstable region, instability parameter is necessary. The instability parameter is given by the expression as shown below

$$\xi\left(\dot{\varepsilon}\right) = \frac{\partial ln \frac{m}{m+1}}{\partial ln \,\dot{\varepsilon}} + m \tag{5.7}$$

The condition for instability is given by the dimensionless instability parameter as given below

$$\xi\left(\dot{\varepsilon}\right) = \frac{\partial ln \frac{m}{m+1}}{\partial ln \,\dot{\varepsilon}} + m \qquad \leq 0 \tag{5.8}$$

Dimensionless stability parameter varies with the strain rate and temperature, and it constitutes an instability map in the processing map of deformation process. The negative value of the instability parameter in the contour map shows the flow unstable region. The plotted contour maps are used to identify the unstable region with the help of stability conditions  $(0 \le \eta \le 2m)$  and instability conditions  $(2m \le \eta \le 0)$ . These both conditions are applicable for all isothermal hot deformation testing for every stress and strain values.

## **5.3.2.4** Temperature sensitivity Parameter (s)

Temperature sensitivity parameter and its partial derivative with respect to strain rate gives the information about the safe region for further mechanical processing of the given material. Temperature sensitivity parameter and its partial derivative with respect to strain rate are given by the following equations

$$s = \frac{\partial \ln \sigma}{\partial \left(\frac{1}{T}\right)} \quad , \quad \dot{s} = \frac{\partial s}{\partial \ln \dot{\epsilon}} \tag{5.9}$$

One more parameter which is also used to plot the contour map and identify the safe region for mechanical processing is the partial derivative of strain rate sensitivity parameter with respect to strain rate and it is given by the following equation

$$\dot{m} = \frac{\partial m}{\partial \ln \dot{\varepsilon}} \tag{5.10}$$

The DMM model gives criteria for the safe region for homogenous deformation or stable plastic flow during further mechanical processing at high temperature which is based on the value of above said parameter as given below:

$$\dot{m} < 0, 0 < m < 1, s \ge 1, \dot{s} \le 0$$
 (5.11)

The contour maps of the processing efficiency of the studied HEA which are based on the DMM model are shown in **fig. 5.8** at the strain of 0.65. **Fig. 5.8(a)** showing the contour maps in which flow instability parameter is superimposed with the power efficiency and it is giving the information about the stable region and unstable region. It is reported that the higher efficiency showing the better workability of the material. On the base of efficiency with the strain rate and high temperature, four domains named as Domain A, Domain B, Domain C and Domain D have been marked as shown in **fig. 5.8(a)**. In **fig. 5.8(a)**, the black lines represent the variation of power efficiency with the variation of strain

rate and working temperature. For the studied HEA, it is clear from the fig. 5.8(a) that the higher power efficiency (30 - 44%) is observed in the strain rate range from  $10^{-2}$  s<sup>-1</sup> to 1 s<sup>-1</sup> and the temperature range from 1150 K to 1350 K and this domain is named as Domain C. It is clear from the fig. 5.8(a) that two regions are of the medium power efficiency lies between 17% to 24% and these domains are observed in the strain rate range from  $10^{-2.5}$  s<sup>-1</sup> to  $10^{-1.5}$  s<sup>-1</sup> and the temperature range from 1125 K to 1200 K and this domain is named as Domain B and another domain which is named as Domain D is observed in the strain rate range from  $10^{-2.5}$  s<sup>-1</sup> to  $10^{-1.5}$  s<sup>-1</sup> and the temperature range from 1300 K to 1350 K. The flow instability parameter is observed in the strain rate range from  $10^{-1}$  s<sup>-1</sup> to 1 s<sup>-1</sup> and the temperature range from 1050 K to 1150 K and this domain is named as Domain A as shown in **fig. 5.8(a).** The domain which has low temperature and high strain rate is defined as unstable region and these regions are avoided for the further thermal mechanical processing. From the **fig.5.8(a)**, it is clear that the stable regions show the efficiency near to 30 % and the iso-efficiency is increasing with the increasing of temperature at a constant strain rate. The maximum efficiency of the studied alloy is 44% in the temperate range from 1300 K to 1350 K and strain rate range from 10<sup>-1</sup> S<sup>-1</sup> to 1 S<sup>-1</sup>. Different domains for the stable and unstable regions for the further thermo physical processing with the different parameters are shown in table 5.1.

The contour maps of the studied single-phase FCC HEA with the variation of strain are shown in **fig. 5.9. Fig. 5.9** gives the information about the stability region with the deformation. It suggests that when the deformation takes place, some higher efficient regions are vanished, and some lower efficient regions become higher efficient regions. From **fig. 5.9(a)**, we can say that at strain 0.1, the highest efficiency is 30% and the stability regions are in the temperature range from 1125K-1230K and strain rate range varies from  $10^{-3}$  s<sup>-1</sup> to  $10^{-2}$  s<sup>-1</sup>. With this region, one more stable region is in the temperature range from 1250 K- 1325K and the strain range vary from and  $10^{-2}$  s<sup>-1</sup> to 1 s<sup>-1</sup>. When the deformation accumulates in the specimen as at 0.4 strain, the stability regions are

changed. **Fig. 5.9(d)** shows the stability regions as temperature vary from 1150 K- 1325 K and strain range varies from  $10^{-2}$  s<sup>-1</sup> to 1 s<sup>-1</sup>. These regions are different from the regions which are shown at strain 0.1. According to the **fig. 5.9(e) & (f)**, at the higher strains, the stability regions are almost same as temperature range from 1150 K- 1325 K and strain range vary from  $10^{-2}$  s<sup>-1</sup> to 1 s<sup>-1</sup>. So, it is crucial to generate the processing maps at higher strains to recognize the safe regions for further thermo mechanical processing. Therefore, the processing maps are generated at strain value of 0.65 to analyse the deformation behaviour of studied HEA.



Fig.5.8 Processing map at strain 0.65 (a) maps for power dissipation efficiency superimposed with instability parameter (b) strain rate sensitivity (c) Rate of change of strain rate sensitivity with respect to strain rate (d) s (e) *s*

DMM	Stable Regions		Unstable Regions	
Parame	Temperature	Strain Rate	Temperature	Strain Rate
ters	Range	Range	Range	Range
М	All	All	No	No
η	1150 K-1300	$10^{-2} \mathrm{s}^{-1}$ to $1 \mathrm{s}^{-1}$	1073 K - 1150	All
	Κ		Κ	
	1300 K - 1323	$10^{-3} \mathrm{s}^{-1}$ to $10^{-3} \mathrm{s}^{-1}$ &	1150 K - 1225	$10^{-3}  \mathrm{s}^{-1} - 10^{-1}  \mathrm{s}^{-1}$
	Κ	$10^{-1}  s^{-1}$ to $1  s^{-1}$	К	
			1225 K - 1300	$10^{-3}  \mathrm{s}^{-1} - 10^{-2}  \mathrm{s}^{-1}$
			Κ	
			1300 K - 1323	$10^{-2}  \mathrm{s}^{-1} - 10^{-1}  \mathrm{s}^{-1}$
			Κ	
$\dot{m} < 0$			1150  K - 1200	$10^{-1.25}  \mathrm{s}^{-1} -$
			Κ	10 <sup>-0.75</sup> s <sup>-1</sup>
			1225 K - 1300	10 <sup>-2.25</sup> s <sup>-1</sup> –
			Κ	10 <sup>-1.75</sup> s <sup>-1</sup>
			1300 K - 1323	$10^{-1.25}  \mathrm{s}^{-1} -$
			Κ	10 <sup>-0.75</sup> s <sup>-1</sup>
$s \ge 1$			1073 K - 1100	10 <sup>-1</sup> s <sup>-1</sup> -
			Κ	1 s <sup>-1</sup>
$\dot{s} \leq 0$			1125 K - 1200	$10^{-1.25}  \mathrm{s}^{-1} -$
			Κ	10 <sup>-0.75</sup> s <sup>-1</sup>
			1225 K - 1300	10 <sup>-2.5</sup> s <sup>-1</sup> –
			Κ	10 <sup>-1.75</sup> s <sup>-1</sup>
			1300 K – 1323	10 <sup>-1.25</sup> s <sup>-1</sup> -
			Κ	10 <sup>-0.75</sup> s <sup>-1</sup>

 Table 5.1. Details of the Stable and unstable regions on the base of
 different parameters



**Fig 5.9** Processing map for Efficiency of power dissipation at different strain value such as (a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4 (e) 0.5 and (f) 0.6

### 5.3.3 Microstructural characterization of hot deformed HEA

For the correlation of the observe data from the processing maps, the microstructure characterization study of the deformed samples is done at different temperatures and strain rates for the studied multicomponent single-phase HEA. The SEM images of the deformed samples are shown in **fig. 5.10**.

**Fig.5.10** shows the microstructure of the stable regions (Domain C). The microstructure of the deformed samples which were tested at 1173 K, 1273 K & 1323 K at the strain rate of  $10^{-1}$  s<sup>-1</sup> showing the crack free microstructure which is correlated the stable regions predicted by the processing maps. **Fig.5.11** shows the microstructure of the unstable regions (Domain A). The microstructure of the deformed samples which were tested at 1173 K at the different strain rates of  $10^{-2}$  s<sup>-1</sup> &  $10^{-1}$  s<sup>-1</sup>.

Instability mechanism is explained by the presences of cracks or localized plastic flow as reported by Sumanta et al. [161] The microstructures showing in the **fig. 5.11** are showing the cracks and localized plastic flow near the pores which are correlated with the prediction of processing maps. The microstructures of the unstable regions (Domain B & Domain D) are also shown in **fig.5.12**. The microstructures of the deformed samples which were tested at 1173 K, 1273 K & 1323 K at the strain rate of  $10^{-2}$  s<sup>-1</sup> are showing the cracks and localized plastic flow. These cracks confirm the prediction of the processing maps in a well manner and these regions are called unstable region for the further thermo mechanically processes.



**Fig 5.10** Scanning electron microscopy micrograph of studied single phase HEA, deformed at (a) 1173 K (b) 1273 K (c) 1323 K at the strain rate of 10<sup>-1</sup> S<sup>-1</sup>. (a), (b) & (c) are at low magnification and (a'), (b') & (c') are at high magnification



**Fig.5.11** Scanning electron microscopy micrograph of studied single phase high entropy alloy, deformed at 1073 K at the strain rate of (a)  $10^{-2} \text{ s}^{-1}$  (b)  $10^{-1} \text{ s}^{-1}$ . (a) & (b) are at low magnification and (a') & (b') are at high magnification



Fig.5.12 Scanning electron microscopy micrograph of studied single phase high entropy alloy, deformed at (a) 1173 K (b) 1273 K (c) 1323 K at the strain rate of 10<sup>-2</sup> s<sup>-1</sup>. (a), (b) & (c) are at low magnification and (a'), (b') & (c') are at high magnification

The four domains A, B, C & D marked in the processing maps and corresponding microstructural features are shown in **table 5.2**.

**Table 5.2** Correlation between predicted from processing maps and microstructure features at different strain rate and deforming temperature

Domains	Temp.	Strain	Efficiency	Microstructural
	Range(K)	Rate(s <sup>-1</sup> )	(η)	Features
Domain A	1073 - 1125	10 <sup>-3</sup> - 1	2.6 - 17	Large Cracks
Domain B	1125 - 1200	$10^{-2.5} - 10^{-1.5}$	17 - 24	Cracks, Pores
Domain C	1150 - 1323	10-1 - 1	30 - 44	Uniform
				distribution
Domain D	1300 - 1323	10 <sup>-2</sup> - 10 <sup>-1</sup>	17 - 24	Cracks, Pores

**5.3.4** Flow curve prediction using different models

## 5.3.4.1 Modified JC model

The flow stress-strain curve obtained from the hot deformation study can be used to develop the constitutive equation and material constants to predict the flow stress behaviour. This model can be used for different material and a large range of temperature and strain rate due to the simplicity of the model and easily availability of the parameters. The modified JC model is used to characterize the flow stress behaviour of the studied HEA under the different deformation temperatures (1073 K, 1173 K, 1273 K, 1323 K) and different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup>, 1 s<sup>-1</sup>). The modified JC model with the relationship of flow stress, temperature, strain, and strain rate can be represented as shown below:

$$\sigma = (A_1 + B_1 \epsilon + B_2 \epsilon^2) (1 + C_1 \ln \dot{\epsilon}^*) \exp\left[(\lambda_1 + \lambda_2 \ln \dot{\epsilon}^*) T^*\right]$$
(5.12)

Where  $\sigma$  is the equivalent flow stress,  $\epsilon$  is the plastic strain,  $\dot{\epsilon}$  is the strain rate, A<sub>1</sub>, B<sub>1</sub>, B<sub>2</sub>, C<sub>1</sub>,  $\lambda_1$  and  $\lambda_2$  are the material constants.

In equation 1,  $\dot{\epsilon}^*$  & T\* is the reference strain rate and reference temperature and it is expressed by

$$\dot{\epsilon}^* = \frac{\dot{\epsilon}}{\dot{\epsilon}_{ref}} \tag{5.13}$$

 $T^* = T - T_{ref}$ 

Where,  $\dot{\epsilon}$  is the strain rate,  $\dot{\epsilon}_{ref}$  is the reference strain rate, T is the deformation temperature and T<sub>ref</sub> is the reference temperature

Now, a reference temperature and a reference strain rate are selected as 1050 °C (1323 K) and 1 s<sup>-1</sup> and the material constants are calculated as given below:

First of all,  $A_1$ ,  $B_1$ , and  $B_2$  are calculated with the help of a polynomial plot between stress and strain at the reference temperature and reference strain rate as shown in **fig. 5.13** (a)

After that  $C_1$  is calculated with the help of the slope of a fitted polynomial curve between  $\sigma/(A_1+B_1\epsilon + B_2\epsilon^2)$  and ln as shown in **fig. 5.13 (b)** 

After that  $\lambda_1$  and  $\lambda_2$  were also calculated according to the given expression as shown in **fig. 5.13 (c)** 

After calculating all material constants, now the predicted flow stress equation is expressed as given below:

 $\sigma_{\text{pred.}} = (183.4 + 202.18\epsilon - 173.05\epsilon^2) \quad (1 + 0.09868 \ln \dot{\epsilon}^*) \quad \exp [(-0.00318 + 4.82 \text{E}^{-4} \ln \dot{\epsilon}^*) \text{ T}^*] \quad (5.15)$ 

Predicted stress for the different temperature and strain rates is calculated with the help of **equation 5.15** and compared with the experimental flow stresses. **Fig.5.14** shows the comparison between predicted flow stress (represented by dashed lines) and the experimental flow stress (represented by solid lines) at the different hot working conditions and strain rate with the help of developed modified JC model. **Fig. 5.14** shows that the modified JC model is successfully applied for the multi-component single-phase HEA at elevated temperature.



**Fig.5.13** Material constants calculation curve (a) Stress Vs. Strain curve at reference conditions for  $A_1$ ,  $B_1$  and  $B_2$  (b)  $\sigma/(A_1+B_1\epsilon+B_2\epsilon^2)$ Vs.  $ln\dot{\epsilon}^*$  curve for  $C_1$  (c)  $\lambda$  ( $\lambda_1+\lambda_2$   $ln\dot{\epsilon}^*$ ) Vs.  $ln\dot{\epsilon}^*$  curve for  $\lambda_1$  and  $\lambda_2$ 



**Fig.5.14** Comparison between Predicted (represented by dashed lines) and experimental (represented by solid lines) flow curve using modified JC model at different temperature and strain rate (a)  $\dot{\varepsilon} = 1 S^{-1}$  $^{1}(b) \dot{\varepsilon} = 0.1 S^{-1}(c) \dot{\varepsilon} = 0.01 S^{-1}(d) \dot{\varepsilon} = 0.001 S^{-1}$ 

### 5.3.4.2 Modified ZA model

The constitutive equation of this model predicts the flow stress by considering the effect of strain and strain hardening on the flow stress. The prediction is completed on the base of dislocation mechanism. The modified ZA model is used to characterize the flow stress behaviour of the studied HEA under the different deformation temperatures (1073 K, 1173 K, 1273 K, 1323 K) and different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup>, 1 s<sup>-1</sup>). The modified ZA model can be represented as shown below:

$$\sigma = (C_1 + C_2 \varepsilon^n) \exp \{ (C_5 + C_6 T^*) \ln \dot{\varepsilon}^* - (C_3 + C_4 \varepsilon) T^* \}$$
(5.16)

Where  $\sigma$  is the equivalent flow stress,  $\epsilon$  is the plastic strain,  $\dot{\epsilon}$  is the strain rate and C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub> & n are the constants. In the **equation 5.16**,  $\dot{\epsilon}^*$  & T\* is the reference strain rate and reference temperature and it is expressed the same as shown in **equations (5.13)** & (**5.14**). Now, a reference temperature and a reference strain rate are selected as 1050 °C (1323 K) and 1 s<sup>-1</sup> and the material constants are calculated with the help of hot deformation experimental stress-strain results by following the procedure as given below:

First of all,  $C_1$  is calculated as 152.67 MPa which is a yield stress value from the stress-strain curve at the reference temperature and reference strain rate.

At the reference strain rate, equation 5.16 can be written as

$$\sigma = (C_1 + C_2 \varepsilon^n) \exp\left\{-(C_3 + C_4 \varepsilon) T^*\right\}$$
(5.17)

After taking the natural logarithm of the equation 5.17

$$\ln \sigma = \ln \left( C_1 + C_2 \varepsilon^n \right) - \left( C_3 + C_4 \varepsilon \right) T^*$$
(5.18)

For the calculation of  $C_3$  and  $C_4$ , two new terms are defined with the help of **equation 5.18** as shown below:

$$I_1 = \ln (C_1 + C_2 \varepsilon^n) \& S_1 = C_3 + C_4 \varepsilon$$
(5.19)

To evaluate the value of  $C_2$ ,  $C_3$ ,  $C_4$  & n material constant, equation 5.19 is used and the calculated value of these constants are 125.63, 0.000932,

0.00489 & 0.36532 respectively which is shown in **fig. 5.15** (a), (b) & (c). To evaluate the material constants  $C_5 \& C_6$ , equation 5.16 can be rewritten after taking natural logarithm and expressed as

$$\ln \sigma = \ln (C_1 + C_2 \varepsilon^n) - (C_3 + C_4 \varepsilon) T^* + (C_5 + C_6 T^*) \ln \dot{\varepsilon}^*$$
(5.20)

A new term  $S_2$  can be defined as  $S_2 = C_5 + C_6 T^*$ 

Now S<sub>2</sub> can be evaluated from the slope of the curve of  $\ln\sigma$  Vs.  $\ln\dot{e}^*$  which is plotted for the different deformation temperatures (1073 K, 1173 K, 1273 K, 1323 K) at each strain value varies from 0.05 to 0.65 with the interval of 0.05. Now C<sub>5</sub> & C<sub>6</sub> can be calculated from the mean value of the slopes and intercepts of the curve of S<sub>2</sub> Vs. T\* and the calculated value of the C<sub>5</sub> & C<sub>6</sub> constants are 0.18035 & 0.000481 as shown in **fig. 5.15 (d)** 



**Fig.5.15** Material constants calculation curve (a)  $ln\sigma$  Vs. T\* curve (b)  $ln\{exp(I_1)-C_1\}$  Vs.  $ln\varepsilon$  curve for  $C_2$  & n (c)  $S_1$  Vs.  $\varepsilon$  curve for  $C_3$  &  $C_4$ (d)  $S_2$  Vs. T\* curve for  $C_5$  &  $C_6$ 

After calculating all material constants, now the predicted flow stress equation is expressed as given below:

$$\sigma_{\text{pred.}} = (152.67 + 125.63\varepsilon^n) \exp\{(0.18035 + 0.000481T^*) \ln \dot{\varepsilon}^* (0.000932 + 0.000489\varepsilon)T^*\}$$
(5.21)

Predicted stress for the different temperature and strain rates is calculated with the help of equation 5.21 and compared with the experimental flow stresses. Fig.5.16 shows the comparison between

predicted flow stress (represented by dashed lines) and the experimental flow stress (represented by solid lines) at the different hot working conditions and strain rate with the help of developed modified ZA model. **Fig. 5.16** shows that the modified ZA model is successfully applied for the multi-component single-phase HEA at elevated temperature.



**Fig.5.16** Comparison between predicted (represented by dashed lines) and experimental (represented by solid lines) flow curve using modified ZA model at different temperature and strain rate (a)  $\dot{\varepsilon} = 1 S^{-1}$  $^{1}$  (b)  $\dot{\varepsilon} = 0.1 S^{-1}$  (c)  $\dot{\varepsilon} = 0.01 S^{-1}$  (d)  $\dot{\varepsilon} = 0.001 S^{-1}$ 

#### 5.3.4.3 Hyperbolic sine Arrhenius model

Now a days, many researchers are using the constitutive equation to estimate the flow stress behaviour during hot deformation analysis which is based on the hyperbolic sinusoidal Arrhenius model. Arrhenius equation is widely used for the prediction of flow stress is directly related to the deformation temperature and strain rate. During the hot deformation study, the effect of strain rate and temperature is incorporated in a single parameter that is called the Zener-Holloman parameter.

The Zener-Holloman parameter is expressed by

$$Z = \dot{\varepsilon} \exp\left(\frac{Q}{RT}\right) = A_1 \left[\sinh\left(\alpha\sigma\right)\right]^n$$
(5.22)

Where  $\dot{\varepsilon}$  is defined as the strain rate, Q is defined as the deformation activation energy, R is defined as the universal gas constant, T is defined as the deformation temperature,  $\sigma$  is defined as the flow stress and A<sub>1</sub>,  $\alpha$ , n is defined as material constants.  $\alpha$  can be defined as  $\alpha = \frac{\beta}{N}$ 

In equation 5.22, activation energy Q is defined as

$$Q = R \left[\frac{\partial ln\dot{\epsilon}}{\partial \ln[\sinh(\alpha\sigma)]}\right] T \left[\frac{\partial \ln[\sinh(\alpha\sigma)]}{\partial(\frac{1}{T})}\right] \dot{\epsilon} = Rns$$
(5.23)

For the evaluation of these material constants, hot deformation experimental stress-strain data for the studied alloy were used [165]. Material constants are calculated at the strain of 0.5 according to the following procedure:

First of all, to evaluate the constant  $\alpha$ ,  $\beta$  and N are calculated from the slopes of the curves of  $\ln \dot{\epsilon}$  vs.  $\sigma$  and  $\ln \dot{\epsilon}$  vs.  $\ln \sigma$  after linear fit which are plotted for the different deformation temperatures (1073 K, 1173 K, 1273 K, 1323 K) and the mean value of  $\beta$  and N are calculated as 0.02924 and 7.26, respectively. So, for the studied alloy the value of  $\alpha$ is calculated as 0.004521 which is shown in fig. 5.17 (a) & (b). The second constant n is calculated from the slope of the curve of  $\ln \dot{\epsilon}$  Vs. ln  $[\sinh (\alpha \sigma)]$  which is plotted for the different deformation temperatures (1073 K, 1173 K, 1273 K, 1323 K) and the mean value of n is calculated as 4.78 which is shown in fig. 5.17 (c). According to equation 5.23, to evaluate the activation energy, s constant is needed, and it is calculated from the slope of the curve of  $\ln [\sinh (\alpha \sigma)]$  Vs. 1/T which is plotted for the different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup>, 1 s<sup>-1</sup>) and the mean value of the s is calculated as 1.11 which is shown in fig. 5.17 (d). Now we can calculate the activation energy directly from equation 5.23 and the value of activation energy is calculated as 441.926 KJ/mol.

By taking the log of the **equation 5.22**, the new equation for the Zener-Holloman parameter is expressed by

$$\ln Z = \ln A_1 + n. \ln [\sinh (\alpha \sigma)]$$
(5.24)

Now, the material constant  $A_1$  can be calculated from the intercept of the curve of lnZ Vs. ln [sinh ( $\alpha\sigma$ )] and the calculated value of  $A_1$  is 1.41E+17. All the material constants are calculated at the strain of 0.5. By following the above-said procedure, all the material constants can be calculated at all strain values from 0.05 to 0.65 in the interval of 0.05. **Fig.5.18** shows the variation of the material constants with the strain.



**Fig.5.17** Material constants calculation curve at the strain of 0.5 (a) ln $\notin$  Vs. stress curve for  $\beta$  (b) ln $\notin$  Vs. ln $\sigma$  curve for N (c) ln $\notin$  Vs. ln [sinh  $(\alpha\sigma)$ ] curve for n (d) ln [sinh  $(\alpha\sigma)$ ] Vs. 1/T curve for s

Equation 5.22 can be rewritten as

$$\sigma = \frac{1}{\alpha} \ln \left[ \left( \frac{Z}{A_1} \right)^{\frac{1}{n}} + \left\{ \left( \frac{Z}{A_1} \right)^{\frac{2}{n}} + 1 \right\}^{\frac{1}{2}} \right]$$
(5.25)

Flow stress is calculated using **equation 5.25** under the different deformation temperatures (1073 K, 1173 K, 1273 K and 1323 K) and different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup> and 1 s<sup>-1</sup>) and compared with the experimental flow stresses. **Fig. 5.19** shows the comparison between predicted flow stress (represented by dashed lines) and the experimental flow stress (represented by solid lines) at the different hot working conditions and strain rate with the help of developed hyperbolic sine Arrhenius model. **Fig. 5.19** shows that the hyperbolic sine

Arrhenius model is successfully applied for the multi-component singlephase HEA at elevated temperatures.



**Fig.5.18** Variation of the material constants with the strain (a)  $\alpha$  Vs.  $\varepsilon$ (b) Q Vs.  $\varepsilon$  (c) lnA Vs.  $\varepsilon$  (d) n Vs.  $\varepsilon$ 



**Fig.5.19** Comparison between Predicted (represented by dashed lines) and experimental (represented by solid lines) flow curve using hyperbolic sine Arrhenius model at different temperature and strain rate (a)  $\dot{\varepsilon} = 1 \text{ s}^{-1}$  (b)  $\dot{\varepsilon} = 0.1 \text{ s}^{-1}$  (c)  $\dot{\varepsilon} = 0.01 \text{ s}^{-1}$  (d)  $\dot{\varepsilon} = 0.001 \text{ s}^{-1}$ 

### 5.3.4.4 ANN model

An artificial neural network is a computational model which is inspired by biological neurons to deal with complex problems such as optimization problems, prediction of unknown data etc. The ANN model is formed from the hundred single units which are called processing elements and each element has input, information transfer function and one output [166]. The ANN model is used in the applications of material engineering such as prediction of flow stresses during hot deformation, prediction of the properties of the materials etc. This model has three types of layers named input layers, hidden layers and output layers. Reliance et. al. [132] is reported the prediction of hot deformation behaviour of Co-Cr-Fe-Ni-Zr quasi peritectic high entropy alloy using ANN modelling in the temperature range varies from 1073 K to 1323 K and strain rate variation is from 0.001 to 10 s<sup>-1</sup>. The flow stress behaviour at different hot working conditions is predicted using the ANN model by taking the experimental data obtained from the hot deformation testing and training these data to obtain the maximum Rvalue and minimum mean square error during the training of the network. In the present study, the hot deformation behaviour of a singlephase high entropy alloy Fe-Co-Cr-Ni-V-Al have been carried out within the temperature range from 800 °C to 1050 °C (800 °C, 900 °C, 1000 °C and 1050 °C) and the strain rate varies from 0.001 s<sup>-1</sup> to 1 s<sup>-1</sup>  $(0.001 \text{ s}^{-1}, 0.01 \text{ s}^{-1}, 0.1 \text{ s}^{-1} \text{ and } 1 \text{ s}^{-1})$ . It is to be remembered that for the ANN modelling, the input data are temperature, strain and strain rate and the output data is flow stress. Total 208 experimental input-output data are used to predict the flow stress behaviour and to develop the ANN model. The one important thing that should be remembered is that the input and output variables have different dimensions and distinct ranges. Due to this variation of data, there is a poor convergence speed and prediction accuracy of the selected model [167]. Therefore, before applying the data for the training, these data values are reduced to the value between 0 and 1 with the help of feature scaling to maintain the steadiness of the data and to ensure that the input and output variables
are dimensionless and in an approximately same magnitude. The feature scaling of the data set is completed by the following equation

$$X_{\rm fscale} = 0.8 \left( \frac{X - X_{min}}{X_{max} - X_{min}} \right) + 0.1 \tag{5.26}$$

In which  $X_{fscale}$  is the scaled value, X is the experimental value of the input and output variables,  $X_{min} \& X_{max}$  are the minimum and maximum value of the input and output variables. The coefficient of 0.1 & 0.8 using in equation 5.26 is used to narrow the data set. However, the strain rate's value drastically changes, and after scaling, the minimum value is too low, hence this equation is inappropriate for the current situation. Therefore, a different logarithmic equation is used for the scaling of the strain rate data and that used equation is given below:

$$\dot{\varepsilon}_{\text{fscale}} = \frac{(\log \dot{\varepsilon} - \log \dot{\varepsilon}_{min})}{(\log \dot{\varepsilon}_{max} - \log \dot{\varepsilon}_{min})} 0.8 + 0.1$$
(5.27)

After a lot of hit and trial method, an optimal structure for the ANN modelling was found and the optimal structure is 3-10-1 where 3, 10 and 1 are the neurons in the input layer, hidden layer and output layer respectively. This optimal structure is shown in **fig. 5.20** (a). **Fig. 5.20** (b) shows that the minimum mean square error ( $MSE_{min}$ ) is obtained in case of 10 neurons in the hidden layer. The  $MSE_{min}$  is  $6.402* 10^{-5}$  at epoch 11. The best correlation coefficient between predicted and experimental flow stress data is also obtained in case of 10 neurons in the hidden layer (as shown in **fig. 5.20**(c)). The correlation between predicted and experimental flow stress data during training, validation, testing and overall is shown in **fig. 5.20**(c).

Flow stress is calculated using developed ANN model under the different deformation temperatures (1073 K, 1173 K, 1273 K and 1323 K) and different strain rates (0.001 s<sup>-1</sup>, 0.01 s<sup>-1</sup>, 0.1 s<sup>-1</sup> and 1 s<sup>-1</sup>) and compared with the experimental flow stresses. **Fig. 5.21** shows the comparison between predicted flow stress (represented by dashed lines) and the experimental flow stress (represented by solid lines) at the different hot working conditions and strain rate with the help of developed ANN model. **Fig. 5.21** shows that the ANN model is

successfully applied for the multi-component single-phase HEA at all temperatures and strain rate ranges.



Fig.5.20 (a) Optimal structure and schematic representation of theANN model (b) MSE convergence during the training and developingANN model (c) Correlation between predicted and experimental flowstress data for training, validation, testing and overall data



**Fig.5.21** Comparison between predicted (represented by dashed lines) and experimental (represented by solid lines) flow curve using ANN modelling at different temperature and strain rate (a)  $\dot{\varepsilon} = 1 \ s^{-1}(b) \ \dot{\varepsilon} =$  $0.1 \ s^{-1}(c) \ \dot{\varepsilon} = 0.01 \ s^{-1}(d) \ \dot{\varepsilon} = 0.001 \ s^{-1}$ 

#### 5.3.4.5 Comparison of different models

It is necessary to compare the predicted results by different models with the experimental results to check the accuracy and correlation and to select the best model for the prediction of flow stress behaviour at different temperatures and strain rates. Therefore, the performance of different used models is evaluated two parameters. The first parameter is the correlation coefficient which is represented by R and second parameter is average absolute relative error (AARE). The both parameters (R and AARE) can be calculated by the expression as given below:

$$R = \frac{\sum_{i=1}^{N} (\sigma_{ef}^{i} - \overline{\sigma_{ef}}) * (\sigma_{pf}^{i} - \overline{\sigma_{pf}})}{\sqrt{\sum_{i=1}^{N} (\sigma_{ef}^{i} - \overline{\sigma_{ef}})^{2} * \sum_{l=1}^{N} (\sigma_{pf}^{i} - \overline{\sigma_{pf}})^{2}}}$$
(5.28)

AARE = 
$$\frac{1}{N} * \sum_{i=1}^{N} \frac{(\sigma_{ef}^{i} - \sigma_{pf}^{i})}{\sigma_{ef}^{i}} * 100$$
 (5.29)

Where, ef is stand for experimental flow and pf is stand for predicted flow. It means  $\sigma_{ef}^{i}$  and  $\sigma_{pf}^{i}$  are the representation of experimental flow stress and predicted flow stress,  $\overline{\sigma_{ef}}$  and  $\overline{\sigma_{pf}}$  are the mean value of experimental flow stress and predicted flow stress and N is the total number of datasets which are used for the modelling. The R and AARE value for the different modelling are shown in table 6.3 and the performance of the different models are compared and shown in **fig. 5.22.** It is clear from the **Fig. 5.22** and **Table 5.3** that the ANN model is the best and accurate model for the prediction of flow stress behaviour for a wide range of temperatures and strain rates with 1.55 % AARE and 0.9988 correlation coefficient.



Fig. 5.22 Performance of different models (a) Modified ZA model (b) Modified JC model (c) Hyperbolic-sine Arrhenius model (d) ANN model

S.No.	Model	AARE	Correlation		
		(%)	Coefficient (R)		
1.	Modified ZA model	31.91 %	0.494		
2.	Modified JC model	22.26%	0.9332		
3.	Hyperbolic-sine Arrhenius model	7.06%	0.9692		
4.	ANN model	1.55%	0.9988		

 Table 5.3 Performance and comparison of the different models

### 5.4 Summary

On the base of the detailed analysis and the discussions, the following points can be summarized as given below:

- I. The hot deformation behaviour of the 6-component studied single phase HEA is successfully completed at different temperature (800°C to 1050°C) and strain rate range  $(10^{-3} \text{ S}^{-1} 1 \text{ S}^{-1})$  by conducting the hot deformation compression test with the help of Gleeble thermo mechanical simulator.
- II. The hot deformation behaviour is successfully correlated with the help of EBSD analysis.

- III. The instability of the studied alloys for the further processing is identified as 1073 K -1125 K with the whole strain range vary from  $10^{-3}$  s<sup>-1 –</sup> 1 s<sup>-1</sup>. With these regions, there are some more regions for the instability are also identified as (Temperature range 1300 K 1323 K, strain rate range  $10^{-2}$  s<sup>-1</sup>  $10^{-1}$  s<sup>-1</sup>) and (Temperature range 1125 K 1200 K, Strain rate range  $10^{-2.5}$  s<sup>-1</sup>  $10^{-1.5}$  s<sup>-1</sup>).
- IV. The processing efficiency of the studied high entropy alloy is 44%.
- V. The optimum stable region for the further hot workability is successfully predicted with the help of processing maps which are generated using DMM modelling.
- VI. The optimum parameters for the further thermal mechanical processing lie in the temperature range 1150 K 1323 K and strain rate range 10<sup>-1</sup> s<sup>-1</sup> 1 s<sup>-1</sup>.
- VII. The ANN model is the best and accurate model for the prediction of flow stress behaviour for a wide range of temperatures and strain rates with 1.55 % AARE and 0.9988 correlation coefficient.

## **Chapter 6**

# Design and development of FeCoNiCrVAITa EHEAs

#### **6.1 Introduction**

EHEAs with seven components (Fe, Co, Ni, Cr, V, Al, and Ta) were designed and developed via vacuum arc melting route guided by the predictions obtained from ANSYS Fluent and ThermoCalc simulations. The simulation results explained that the time period for solidification was increased from 0.16 sec to 0.19 sec with the addition of Ta. The solid-liquid interface advancement and the cooling curve slope at twophase existence were linear and having different slopes by changing the Ta content. The phase evolution was predicted using CALPHAD approach which show that when 10 at% Ta is added, the microstructure is changed from hypoeutectic to hypereutectic with the presence of FCC and Laves phases. The experimental results also show the presence of eutectic mixture (L  $\rightarrow$  FCC + Laves) of ductile FCC phase and hard Laves phase. The mechanical properties such as tensile strength, yield strength and microhardness of the studied alloys are increased from 828 MPa, 494 MPa, 204.67 HV to 1257 MPa, 1140.5 MPa, and 651.4 HV with the slight reduction of % elongation from 47.6% to 28.5% with the addition of Ta from 2.5% to 10%. The experimental results corroborate with the predicted results using thermodynamic simulation and numerical simulation by ANSYS Fluent software.

#### **6.2 Objectives**

- To design and develop the 7 components EHEAs (FCC + Intermetallic) with the help of integrated approach of combining thermodynamic simulation, numerical simulation, and solidification processing technique.
- To investigate the phase equilibria study experimentally and compared with the thermodynamic simulation.
- To investigate the solidification behaviour of designed EHEAs using developed solidification simulation model.

• To evaluate the mechanical properties of the designed HEAs and correlated with the numerical simulation results.

#### **6.3 Simulation and Experimental Procedures**

A transient 2D solidification simulation was developed and solved for EHEAs by using the ANSYS Fluent software. It was used to simulate the solidification behaviour of 7 components novel designed EHEAs to predict the effect of Ta. A desktop computer equipped with i7 intel core processor and 32 GB RAM was used to conduct the whole simulation procedure. The simulation is carried out by adding the thermophysical properties and different operating conditions. Optimum mesh size and time step have been selected on the base of mesh independence and time independence study of the developed model (as mentioned in chapter 5). The FeCoNiCrVAITa<sub>x</sub> EHEAs were prepared by vacuum arc melting cum suction casting unit using appropriate amount of the different elements with the purity level of more than 99.9%. The cast ingots were remelted 5 times to obtain the homogenous mixture of the studied alloys. The casted buttons were remelted in the suction casting unit and solidified in a cylinder copper mould cavity of 6 mm diameter. The XRD observations were carried out to identify the formation of phases during solidification. The evolution of the microstructures during the solidification of the studied EHEAs were observed by FE-SEM attached with EDS. The microhardness of the studied alloys and the effect of Ta on the microhardness were calculated with the help of MMV-A microhardness tester under a constant load of 500g for a dwell time of 30 sec with an indentation speed of  $30 \,\mu$ m/s. The five different readings of microhardness were taken, and the average values were selected for observation. For tensile testing, flat specimens were prepared by using wire EDM. The mechanical properties were calculated by using UTM by using the polished flat tensile samples as mentioned in ASTM standards.

#### **6.4 Results and Discussion**

#### 6.4.1 Thermodynamic simulation

During the solidification, the evolution of phases in the investigated EHEAs with the addition of Ta were predicted with the help of thermodynamic simulation using the ThermoCalc version 2021b with TCHEA4 database. The pseudo FeCoCrNiVAl-Ta binary phase diagram is calculated by using ThermoCalc software as shown in fig. **6.1**. It shows the evolution of different phases at different content of Ta in the studied EHEAs. It suggests that with the addition of Ta content, eutectic phase (FCC + Laves Phase) formation is continue increasing. It shows that when the alloy has a hypo-eutectic composition, the proeutectic phase has an FCC crystal structure, however when the alloy has a hyper-eutectic composition, the proeutectic Laves phase occurs. In the phase diagram, the eutectic composition point is 8.7 at% and therefore, we designed  $Fe_{20-X}CoNiCrVAITa_X$  (X = 2.5%, 5%, 7.5% and 10%) HEAs whose composition are around the maximum solubility, hypoeutectic, near eutectic and hyper eutectic, respectively. The solidification pathways were predicted with the help of scheil's solidification curves as shown in fig.6.2. Fig. 6.2 (a) shows the scheil's solidification curve in hypoeutectic side composition (i.e., Ta 5 at%) and it is showing the formation of primary FCC solid solution phase followed by the formation of eutectic mixture of FCC and laves phase. Fig. 6.2 (b) shows the scheil's solidification curve in hypereutectic and near eutectic side composition (i.e., Ta 10 at%) and it is showing the formation of primary laves phase followed by the formation of eutectic mixture of FCC and laves phase.

#### 6.4.2 Phase Equilibria study of designed EHEAs

The evolution of different phases during the solidification has been analysed with the help of X-ray Diffractometer (XRD), field emission scanning electron microscopy (FE-SEM) attached with the electron dispersive spectroscopy (EDS). The phase transformation temperatures with the evolution of the different phases and thermal stability have been identified with the help of differential scanning calorimetry (DSC) analysis. The detailed analysis of the phase equilibria study is given below:



Fig.6.1 Phase Diagram with the variation of Ta content obtained from

ThermoCalc software



**Fig.6.2** Scheil's solidification pathways for (a) Ta<sub>5</sub> (b) Ta<sub>10</sub> obtained from ThermoCalc software

#### 6.4.2.1 Structural characterization

The presence of phases and their crystal structure were identified with the help of XRD. The XRD micrograph of the studied alloys is shown in **fig. 6.3**. The XRD micrograph exhibits the mixture of FCC phase and Laves phase which coincides the pseudo phase diagram and confirms the ThermoCalc results. **Fig. 6.3** confirm the formation of eutectic mixture with the addition of Ta in the single-phase HEA. It is clear from the figure that the number of peaks and intensity of the laves phase is continue increases with the addition of Ta and it is showing the eutectic formation of the studied alloys.



Fig 6.3 XRD micrographs of the studied component EHEAs

#### 6.4.2.2 Microstructure Characterization

The microstructure characterization of the investigated EHEAs were carried out with the help of FESEM with BSE mode. The morphologies of the developed EHEAs in low and high magnification are shown in fig.6.4. The presence of the different phases in the investigated EHEAs are marked (as shown in fig.6.4) with the help of EDS results attached with FESEM. It can be observed from fig. 6.4 that the microstructure changes take place from hypoeutectic microstructures to hypereutectic with the addition of Ta from 2.5 at% to 10 at%. Fig. 6.4 (a to c) show that the presence of proeutectic dendrite FCC phase and the eutectic mixture between laves phase and FCC phase with the increment of volume fraction of laves phase. The microstructure with Ta 10 at% having proeutectic laves phase and eutectic matrix between laves phase and FCC phase as shown in fig. 6.4(d). The elemental analysis was confirmed with the help of EDS and the EDS results (as shown in table 6.1) confirm that the FCC solid solution phase is enriched in Fe, Co and Ni and laves phase is enriched in Ta.



Fig 6.4 SEM Micrographs with (a) Ta<sub>2.5</sub>, (b) Ta<sub>5</sub>, (c) Ta<sub>7.5</sub>, (d) Ta<sub>10</sub> for 7 components EHEAs respectively

# Table 6.1 EDS analysis of the designed EHEAs FeCoCrNiVAlTa<sub>X</sub> (X

Alloys	Phases	(at%)						
		Fe	Co	Ni	Cr	V	Al	Та
FeCoCr	Nominal	17.5	25	25	20	5	5	2.5
NiVAlT	FCC	15.8	24.5	25.6	20	5.45	6	2.5
a <sub>2.5</sub>	Eutectic	12.9	24	22.9	17.3	5.55	5.35	11.9
FeCoCr	Nominal	15	25	25	20	5	5	5
NiVAlT	FCC	16.7	26.3	25.3	22.1	5	2.6	2
a5	Eutectic	13.4	24.9	23.4	20.6	5.6	2.4	9.8
FeCoCr	Nominal	12.5	25	25	20	5	5	7.5
NiVAlT	FCC	13.9	26.9	26.3	22.3	5	2.7	2.8
a7.5	Eutectic	11.8	25.4	25.4	20.2	5.2	2.8	9.3
FeCoCr	Nominal	10	25	25	20	5	5	10
NiVAlT	FCC	9.7	25	29.6	21.5	6.6	4.1	3.6
a <sub>10</sub>	Eutectic	10.4	25.6	22.4	20.8	4.7	3.7	12.4

= 2.5 %, 5%, 7.5% and 10%) with the nominal composition

# **6.4.2.3 Thermal Analysis**

The DSC analysis of the studied EHEAs was conducted to ascertain the phase transformation temperatures. **Fig. 6.5** shows the DSC thermogram of the studied EHEAs. It can be observed that all studied alloys with the

variation of Ta from 2.5 % to 10 % are showing exothermic peaks during the heating cycle at the different temperature which are very close to the predicted values from CALPHAD analysis. The DSC curves show the phase transformation for different phases as FCC solid solution phase and eutectic reactions between FCC and laves phases at different temperatures with the different exothermic peaks as shown in **Fig. 6.5**. In case of Ta<sub>2.5</sub>, the FCC solid solution phase peaks are high compare to the eutectic phase because of the composition which is very near to maximum solubility limit as shown in phase diagram. After the addition of Ta from 5% to 10%, the peaks are showing the formation of FCC and eutectic phase with the increment of eutectic phase. **Fig. 6.5** shows the thermal stability of the developed EHEAs which is approx. 1360 °C. So, these EHEAs are the potential candidates for high temperature applications.



Fig 6.5 DSC analysis of the studied EHEAs with the addition of Ta from 2.5at% to 10at%

# 6.4.3 Comparison of phase equilibria using thermodynamic simulation results and experimental results

Thermodynamic simulation suggests the formation of FCC and Laves phases in the designed EHEAs as shown in **Fig. 6.1 & 6.2.** The XRD patterns of the studied multicomponent alloys also showing the existence of FCC and Laves phases as shown in **Fig. 6.3**. The thermodynamic simulation results can be validated with the help of microstructure analysis of the developed EHEAs. The evolution of different phases during the solidification have been identified with the help of BSE-SEM micrographs attached with EDS analysis. The microstructural analysis shows the formation of FCC and Laves phases as shown in **Fig 6.4**. With the addition of Ta from 2.5% to 10%, the volume fraction of laves phase is continue increasing which also validated the thermodynamic simulation results in a well manner. The DSC analysis of the studied EHEAs also confirm and validate the thermodynamic simulation results in a well manner.

#### 6.4.4 Numerical simulation

#### 6.4.4.1 Initial and Boundary conditions

At initial, the molten metal was poured in the mould cavity at a particular temperature which is 30 K superheat than the melting point of the specific alloy. The temperatures at which the molten metal of investigated EHEAs were poured in the mould cavity are 1660 K, 1615 K, 1602 K and 1568 K with the addition of Ta from 2.5 at% to 10 at% respectively.

#### **6.4.4.2 Thermophysical Properties**

The solidification simulation is carried out using a designed EHEAs. **Table 6.2** lists the thermophysical characteristics of the selected 7 components EHEAs respectively as given below:

#### 6.4.4.3 Liquid Fraction Contours during the solidification

The variation of the liquid fractions contours with the time for studied EHEAs are shown in **fig.6.6**. **Fig. 6.6** show the fraction of liquid at the different instants of the solidification process during suction casting and variation of the solidification time with the addition of Ta in the investigated EHEAs. During the solidification process, the shape and progress of the solidification interface can be easily visualized with the help of contours of the liquid fraction.

The completely solid and liquid states are represented by blue and red colour, respectively. After the molten metal is poured into the mould, heat is transferred from the molten metal to the mould, and the liquid fraction in the mould cavity continues to decrease from red to blue, or

from 1 to 0. As the time elapsed from 0.16 sec to 0.19 sec with the addition of Ta from 2.5 at% to 10% respectively, the solidification process is complete and the liquid fraction in the mould cavity is zero, indicating that the liquid has entirely solidified. The totally solid-state (as depicted in **fig. 6.6(v)**) is indicated by the zero value of the liquid fraction value as specified by the enthalpy porosity technique. The temperature drop is faster in the lower and side regions of the mould and slower in the upper and centre regions of the mould. These phenomena occur due to the more heat transfer as the colder mould comes in contact with the molten metal.

Properties	Units	7 components EHEAs					
		Ta2.5	Ta5	Ta7.5	Ta <sub>10</sub>		
Thermal	W /	128.725	128.15	127.575	127		
Conductivity	m-K						
Specific Heat	J / Kg-	457.825	450.1	442.375	434.65		
Capacity	Κ						
Density	Kg /	7.14	7.34	7.54	7.742		
	m <sup>3</sup>						
Latent Heat	KJ /	315.15	313.35	311.55	309.75		
	Kg						
Viscosity	Kg /	0.005143	0.005205	0.005268	0.00533		
	m-K						
Liquidus	Κ	1635	1590	1577	1543		
Temperature							
Solidus	Κ	1525	1521	1514	1512		
Temperature							

 Table 6.2: Thermophysical properties of the investigated 7

 components EHEAs

These contours can be divided into 9 colours in which dark blue and dark red colour show the complete solid and liquid state of the casting metal respectively and 7 colours starts from light blue colour near the dark blue colour and ended with orange colour near the dark red colour.

On the base of these colours, these contours can be divided into 3 regions in which dark blue and dark red colour show the solid and liquid zone respectively and other colours shows the mushy zone in the casting metal as shown in **fig. 6.7**. It explains the effect of Ta on the amount of the presented phases i.e., the liquid mass fraction value at a particular time of solidification (0.1 sec) is continuously increasing from 0.686 to 0.877 with the addition of Ta from 2.5% to 10% respectively.

# **6.4.4.4** Variation of fraction of liquid with the temperature during the solidification

During the solidification, fraction of the liquid is continue decreasing. Therefore, the variation of fraction of liquid with the temperature during the solidification are shown in fig. 6.8 for the investigated EHEAs at the regular time interval of 0.05 sec (as shown in fig. 6.8(a)), 0.1 sec (as shown in fig. 6.8(b)), 0.15 sec (as shown in fig. 6.8(c)). It is clear from the fig, that the solidification start point comes to lower side with the increment of Ta from 2.5at% to 10 at%. It can be observed from fig. 6.8 that the relationship between temperature and the fraction of liquid are linear, but at 0.15 sec, there is some change in the slope. Fig. 6.8 (c) shows that the slope for Ta<sub>2.5</sub> and Ta<sub>5</sub> are different than Ta<sub>7.5</sub> and Ta<sub>10</sub> for Fe-Co-Ni-Cr-V-Al-Ta<sub>X</sub> EHEAs. The reason behind this phenomenon is due to the formation of near fully eutectic phase or hypereutectic phase in case of Ta<sub>7.5</sub> and Ta<sub>10</sub> compared to the hypoeutectic phase in case of Ta<sub>2.5</sub> and Ta<sub>5</sub> for studied EHEAs. It is noteworthy to mention that the liquid fraction of investigated HEAs is decreasing slowly with the temperature by increasing the Ta content.

#### 6.4.4.5 Contours of temperature during the solidification

The temperature distribution in the casting metal zone at various locations with the variation of time during the solidification process is depicted in **fig. 6.9** for 7 components EHEAs, respectively. The temperature of the casting metal zone continues to drop after the molten metal is poured because heat is transferred from the molten metal to the mould. The temperature profiles with various colour gradients depict the temperature change at various locations in the casting metal zone during

various stages of the solidification process. **Fig. 6.9** indicate that the temperature starts to decrease from the mold side to the inner side after contact with the mold which is at room temperature. It is clear from the **fig.6.9** that it follows the same pattern as shown in the contours of liquid fraction. Dark red colour is high in the case of EHEAs containing Ta 10 at% compared to the Ta 2.5 at%. It is clear that the solidification time is increases with the addition of Ta in the investigated EHEAs.



Fig 6.6 Contour of liquid fraction at (i) 0.01 sec (ii) 0.05 sec (iii) 0.1 Sec (iv) 0.14 sec for all alloys and (v) 0.16 sec, 0.17 sec, 0.18 sec, 0.19 sec for variation of Ta from 2.5 at% to 10 at% respectively. [(A) Ta<sub>2.5</sub>, (B) Ta<sub>5</sub>, (C) Ta<sub>7.5</sub>, (D) Ta<sub>10</sub>]



**Fig.6.7** Contours of the liquid fraction after 0.1 sec of the solidification for (a) Ta<sub>2.5</sub>, (b) Ta<sub>5</sub>, (c) Ta<sub>7.5</sub>, (d) Ta<sub>10</sub> for 7 components





#### 6.4.4.6 Variation of temperature with the distance of mould

During the solidification, the variation of temperature is happened in the mould from the mould wall to the centre of the mould. The variation of temperature at the different instants of solidification within the mould are shown in **fig. 6.10** for different investigated EHEAs. **Fig. 6.10** shows the lowering of the temperature with the solidification and with the addition of Ta content. There is a high temperature in the middle part of the mould (as shown in **fig. 6.10**) which follow the temperature and Liquid fraction profiles. It's also worth noting that the symmetric heat transfer occurs from the centre of the mould to both sides of the walls



Fig.6.9 Contour of temperatures at (i) 0.01 sec (ii) 0.05 sec (iii) 0.1 Sec (iv) 0.14 sec for all alloys and (v) 0.15 sec, 0.16 sec, 0.17 sec, 0.18 sec for variation of Ta from 2.5 at% to 10 at% respectively. [(A) Ta<sub>2.5</sub>, (B) Ta<sub>5</sub>, (C) Ta<sub>7.5</sub>, (D) Ta<sub>10</sub>]

#### 6.4.4.7 Cooling curves during the solidification

The rate of cooling influences the evolution of microstructure and the formation of defects during the solidification. By carefully controlling the cooling rate during the solidification of investigated EHEAs, a sensible range of process parameters can be used to achieve improved metallurgical and mechanical qualities. The crystallization increases with the slow cooling rate and if the rate of cooling is very high then there are chances of defects formation in casting. Therefore, it is necessary to predict the cooling rate behaviour during the solidification with the help of ANSYS Fluent software to obtain a defect free casting.



**Fig.6.10** Temperature vs. distance in the mould during the solidification at different time periods for (a)  $Ta_{2.5}$ , (b)  $Ta_{5}$ , (c)  $Ta_{7.5}$ , (d)



**Fig 6.11** Cooling curves (Temperature vs. time relationship) during the solidification with the addition of Ta content

To investigate the cooling behaviour of the studied EHEAs, the cooling curve or temperature-time relationship for the selected centre part of the mould for 1 sec is shown in **fig. 6.11**. The centre part is selected because the phase change mechanism will be observed where the cooling rate is slow. **Fig. 6.11** shows that the phase change mechanism is observed in the temperature range. The solidification of the investigated alloys

completed in two stages. In the first stage, the phase change mechanism from liquid to solid takes place and the second stage, heat transfer takes place in completely solid state. It can be noticed that the slopes of the cooling curve are different for  $Ta_{7.5}$  &  $Ta_{10}$  compared to the  $Ta_{2.5}$  &  $Ta_{5}$ . The difference in the slope may be due to the presence of near eutectic or hypereutectic microstructure formation as shown in **fig.6.4**. These finding show the good agreement of numerical simulation results with the microstructural features.

#### 6.4.5 Mechanical Properties of designed EHEAs

It is clear from the microstructural analysis that the designed EHEAs having the combination of FCC phase and Laves phase. In the fine eutectic laminar microstructure, ductile FCC phase and hard laves phase are present therefore it is expected that the developed alloys have better mechanical properties with a good combination of ductility and strength. The effect of Ta on the tensile properties of the designed EHEAs is shown in **fig. 6.12**. **Fig. 6.12(b)** shows the continue increment in the ultimate tensile strength from 828 MPa to 1257 MPa with the addition of Ta from 2.5 at% to 10 at% in the designed EHEAs. The lowest yield strength and superior ductility is obtained in case of 2.5% Ta whereas yield strength is continue increasing and ductility is continuously decreasing with the addition of Ta from 2.5 at% to 10 at% in the designed EHEAs (as shown in **fig. 6.12(a and c)**).

The variation in the microhardness with the addition of Ta is shown in **fig. 6.13**. It is clear from the microstructure features that volume fraction of the laves phase is continue increasing with the addition of Ta %. Given that the laves phase is a hard phase, the hardness will increase as its volume fraction increases. With the addition of Ta, the lamellar spacing is also decreases by changing the microstructure from hypoeutectic to hypereutectic and the reduction in lamellar spacing also have some contribution in the increment of hardness. It can be noticed from **fig. 6.13** that the hardness is increasing in a linear way when Ta is added from 2.5 % to 7.5 % but after addition of 10% Ta, the hardness is increased drastically. This phenomenon is happened due to the sharp increment of volume fraction of laves phase in case of 10% Ta. **Fig. 6.13** shows that the hardest alloy among the investigated EHEAs is FeCoCrNiVAlTa<sub>10</sub> and its showing 651.404 HV microhardness compared to the microhardness 204.676 HV with 2.5% Ta.



**Fig.6.12** (a) Tensile engineering stress-strain curve (b) Ultimate tensile strength variation (c) Yield strength variation of the FeCoNiCrVAlTa<sub>X</sub>



Fig. 6.13 Microhardness variation with the effect of Ta in investigated EHEAs

After tensile testing, the scanning electron microscope was used to investigate the fracture properties of the investigated specimen fracture surfaces. The SEM micrographs of the tensile fracture samples are shown in **fig. 6.14**. The dimples structures are found in case of Ta 2.5 % and 5 % as shown in **fig. 6.14 (a, b)** whereas less dimples structure or almost flat structure are found in case of Ta 7.5 % and 10% as shown in **fig. 6.14(c, d)**. **Fig. 6.14** shows the decrement of the ductility with the variation of Ta content from 2.5 % to 10%. **Fig. 6.14 c & d** shows the ductility tear edge and elongated groove microstructure that is called trench like microstructure or river type cleavage microstructure. It means during the tensile deformation; the soft FCC phase is stretched and the FCC phase becoming thinner and hard laves phases with bare deformation of elongated groove microstructure. **Fig. 6.14 a & b** show the highly ductile fracture phenomena whereas **fig. 6.14 c & d** show the mixture of ductile and brittle fracture phenomena compare to the a & b. These phenomena follow the tensile results and ductility behaviour of the investigated EHEAs with the variation of Ta content.



Fig. 6.14 SEM micrographs of tensile fracture surfaces of the investigated EHEAs with variation of Ta (a) 2.5% (b) 5% (c) 7.5% (d) 10%

# 6.4.6 Comparison of the studied HEAs with the reported high strength alloys

The mechanical properties of the studied single phase HEAs and EHEAs have been compared with the other reported alloys such as Steel, Ni based superalloy, Co based super alloy and Fe based superalloy. The comparison of the developed alloys in the present study with the other reported alloys are shown in fig. 6.15 and Table 6.3. Fig. 6.15 shows that the evaluated mechanical properties are higher for the developed alloys in comparison to the other reported alloys.

S.No.	Material	UTS	YS	%E	References
		(MPa)	(MPa)		
1	Stainless Steel AISI 316L	653	534	16.2	[168]
2	Ni based alloy with 2.4Ti	898	660	12	[169]
3	Ni based alloy with 3Ti	984	751	11	
4	247 A Ni based superalloy	900	743	8.35	[170]
5	Co based 0Mo superalloy	690	560	4.2	[171]
6	Co based 5Mo superalloy	630	540	3.8	
7	GH984 Fe based superalloy	989	530	35.5	[172]
8	6c FCC HEA	518	257	64.8	Present
9	7c Ta5 EHEA	911	522	43	work
10	7c Ta10 EHEA	1257	1150	28.5	

**Table 6.3:** Comparison of the present study with the reported work



Fig. 6.15 Comparison of the present study with the reported work

### 6.5 Summary

The main findings of this study can be summarized as follows:

- i. We have successfully designed and developed the EHEAs with the addition of Ta with the promising mechanical properties even in the as-cast alloys.
- ii. The designed FeCoNiCrVAlTa<sub>X</sub> (X = 2.5%, 5% and 7.5%) show the hypoeutectic microstructures whereas FeCoNiCrVAlTa<sub>10</sub> alloy show the hypereutectic microstructure.
- iii. The solidification pathways (L → L + FCC, L → L + laves, L → FCC + laves) obtained from ThermoCalc was confirmed and correlated in well manner with the experimental microstructure features.
- iv. The ANSYS Fluent simulation results explained that the time period from pouring start to freezing end or solidification time was increased from 0.16 sec to 0.19 sec with the variation of Ta from 2.5 at% to 10at% respectively.
- v. The solid-liquid interface development and the cooling curve slopes with the solidification time was linear with the different

slopes as Ta content vary from 2.5% to 10% that affect the mechanical properties of the investigated alloys.

vi. The excellent mechanical properties like tensile strength, yield strength, microhardness and % elongation of FeCoNiCrVAlTa<sub>10</sub> are 1257 MPa, 1140.5 MPa, 651.4 HV and 28.5% respectively compare to the other investigated alloys.

# **Chapter 7**

# **Conclusions and Scope for Future Work**

#### 7.1 Conclusions

The following conclusions may be summarized based on present research work:

- The Al-Ni-X (X = Fe, Cr, Co, V, Ta, and Si) and Al-Cu-X (Ni and Si) multicomponent alloys have been successfully developed using integrated approach of combining thermodynamic simulation and experimental solidification techniques. It is found that the studied multicomponent alloys consist of FCC solid solution phase and one or more intermetallics phases.
- ii. The effect of different alloying elements has been investigated and Al<sub>93</sub>Ni<sub>4</sub>Ta<sub>3</sub> shows the better mechanical properties (UTS ~296 MPa, % Elongation ~ 18% and Microhardness ~284.74 HV) among all studied ternary alloys.
- iii. The HEAs (Single phase HEAs and EHEAs) have been successfully developed by considering the same microstructure features such as FCC solid solution phase or the mixture of FCC solid solution phase and intermetallics.
- iv. The single phase Fe<sub>20</sub>Ni<sub>25</sub>Co<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub> HEA is successfully developed and selected for hot deformation behaviour analysis on the base of better mechanical properties.
- v. A solidification simulation is successfully completed and validated with 1.22% error. The solidification behaviour is predicted and correlated with the mechanical properties.
- vi. The hot deformation behaviour of studied single phase Fe<sub>20</sub>Ni<sub>25</sub>Co<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub> HEA is understood and optimum thermomechanical processing conditions have identified with the help of processing maps.

- vii. The deformation behaviour has been correlated with the grain size distribution and dislocation movements with the help of EBSD analysis.
- viii. The flow stress behaviour at different temperature and strain rates are predicted using different modelling and ANN model shows the good agreement with the experimental results with1.55 % AARE and 0.9988 correlation coefficient.
  - ix. Seven component Fe<sub>20-X</sub>Ni<sub>25</sub>Co<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub>Ta<sub>X</sub> (X = 2.5 at% to 10 at%) have designed and developed using integrated approach. It is found that the studied EHEAs consist the mixture of FCC solid solution phase and Laves phase.
  - x. Finally, EHEA with the unique microstructure (FCC + Intermetallics) show the good balance in mechanical properties in term of strength and ductility as compared to the other developed multicomponent alloys as shown in Fig. 7.1.



**Fig. 7.1** Comparison of mechanical properties of developed multicomponent alloys with unique microstructure (FCC + Intermetallic)

### 7.2 Scope for Future Work

Based upon the studies carried out, related to the subject of different types of high entropy alloys (HEAs) in the present dissertation, a number of research problems could be foreseen.

- It is necessary to study the hot deformation behaviour and processing maps of 7 component Fe<sub>20-X</sub>Ni<sub>25</sub>Co<sub>25</sub>Cr<sub>20</sub>V<sub>5</sub>Al<sub>5</sub>Ta<sub>X</sub> (X = 2.5%, 5%, 7.5% and 10%) EHEAs with nanoscale microstructural features at various temperatures and strain rates in order to comprehend plausible deformation mechanisms and identify the thermomechanical processing conditions for high temperature applicability.
- To comprehend the oxidation kinetics, both isothermal and nonisothermal oxidation experiments of developed single phase HEAs and EHEAs are to be carried out.
- It is necessary to explore the corrosion of developed single phase HEAs and EHEAs in various electrolyte solutions in order to comprehend their corrosive resistance.
- It is necessary to study the tribological behaviour of EHEAs to comprehend how the environment affects their mechanical behaviour.
- Developing and improving of designed HEAs by using different surface modification techniques such as Coating techniques, Friction stir processing etc.

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