STUDIES ON MICROSTRUCTURE, MECHANICAL AND HIGH-TEMPERATURE OXIDATION BEHAVIOUR OF TUNGSTEN CONTAINING HIGH ENTROPY ALLOYS

Ph.D. Thesis

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STUDIES ON MICROSTRUCTURE, MECHANICAL AND HIGH-TEMPERATURE OXIDATION BEHAVIOUR OF TUNGSTEN CONTAINING HIGH ENTROPY ALLOYS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled STUDIES ON **MICROSTRUCTURE, MECHANICAL AND HIGH-TEMPERATURE OXIDATION BEHAVIOUR OF** TUNGSTEN CONTAINING HIGH ENTROPY ALLOYS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2017 to April 2021 under the supervision of Dr Vinod Kumar, Assistant Professor at 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.

signature of the student with date (NAME OF THE PhD STUDENT)

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

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Signature of Phesis Supervisor with date

(Dr. VINOD KUMAR)

Dedicated to: <u>My Parents:</u> Sh. PR Dewangan & Smt. Ganga Bai <u>Brother and sister-in-law & nieces:</u> Sh. Santosh Dewangan & Mrs. Laxmi Dewangan, Kavya & Yashi

&



"The understanding of research isn't the knowledge you gather in your head. It's the masterships you gain about how to acquire and serve the nation for their betterment."

- Sheetal Kumar Dewangan

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Skymon Deningon

(Sheetal Kumar Dewangan)

ABSTRACT

Novel AlCrFeMnNiWx (x= 0, 0.05, 0.1 & 0.5 mol) high-entropy alloys (HEAs) have been synthesized by both powder metallurgy and vacuum arc melting routes. The addition of tungsten on the phase evolution in the spark plasma sintered and arc melted sample was investigated using X-Ray diffractometry (XRD). HEAs' morphology and composition were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. The detailed phase and microstructural characterization of arc melted HEAs reveal the presence of BCC Fe-Cr-Mn-rich (β 1) primary phase and BCC Ni-Al-rich (β 2) secondary dendritic phase. In the powder metallurgy route, during mechanical alloying, solid solution was formed with the formation of major BCC and minor FCC phases fraction in AlCrFeMnNiWx (x=0, 0.05, 0.1 & 0.5 mol) HEAs while additional ordered B2 and σ phases were found after the SPS. The phase stability with respect to temperature has been studied using a differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA). Thermodynamic parameters for AlCrFeMnNiWx alloys are calculated and studied to explain the formation of a solid solution. The formation and growth of the AlFe phase in AlCrFeMnNiWx HEAs have been described schematically, mainly due to the high enthalpy difference between the binary elements. Furthermore, microhardness has been evaluated in alloy systems. In addition, to establish the relation between the alloying composition and hardness values, an artificial neural network (ANN) model has been approached to predict the alloys' hardness with different elemental compositions.

The designed spark plasma sintered HEAs exhibit excellent hardness (8.31 – 13.57 GPa) and high elastic modulus (165.52 GPa - 202.3 GPa), strongly dependent upon the tungsten content while experimented by the nanoindentation. Further, The HEAs are utilized for heat treatment to better understand the alloy behavior due to different processing routes. A set of heat treatments has been performed at 800°C, 1000°C, and 1200°C. HEAs' microstructure and crystal structure have been compared by using a Scanning Electron microscope (SEM) and X-ray diffractometer. This study reveals a drastic change in the morphology in arc melted samples. Admittedly, the spark plasma sintered sample has coarsening appropriately in the presence of tungsten in the alloy system. Afterward, microhardness testing has been performed to understand the alloys' softness behavior. The alloys prepared by different routes have become softer and more homogeneous after heat treatment.

A separate study was also performed to evaluate the possibility of hydrogen storage in the equiatomic high entropy alloy system. A novel high entropy alloy (AlCrFeMnNiW) is synthesized via high-energy planetary ball milling with an average crystallite size of 10.37 nm. The hydrogen storage behavior of this alloy is investigated through the gravimetric method. The hydrogen storage capacity is observed to be 0.615 wt% at atmospheric pressure and temperature. The microstructural characterization of an alloy is carried out utilizing X-Ray diffraction (XRD), scanning electron microscope (SEM), and energy-dispersive X-ray (EDX) analysis to determine its lattice parameters, crystallite size, chemical composition, etc. The unit cell volume of the asprepared alloy is estimated as 0.03131 nm^3 , whereas the average crystallite size decreased by ~10.8% upon hydrogenation. The dehydrogenation of the sample is performed using thermogravimetry analysis (TGA) with different scanning rates. Activation energy during hydrogen desorption is found to be - 8.161 kJ/mol. The enthalpy and entropy of the mixing are estimated to be -2.645 kJ/mol and 1.793 R J/mol K.

For the oxidation study, an extensive experiment has been performed, and every oxidation experiment was repeated to check the reproducibility of the oxidation results. Initially, spark plasma sintered (SPS) AlCrFeMnNiW_x (x = 0, 0.05, 0.1, 0.5 mol) HEA oxidized isothermally at 200°C, 500°C, 700°C, 800°C, and 850°C using thermal gravimetric analyzer (TGA) for 50 hr. XRD, SEM, and Raman spectroscopy were utilized to investigate the oxidized samples. The HEAs exhibited multifarious behavior while adding tungsten and shows the formation of various oxides. Admittedly, alloying constituent significantly affects the oxidation behavior due to complex oxide layers and outstanding oxidation resistance at high temperatures confirms that the proposed HEAs would be applicable for high-temperature applications.

Furthermore, an artificial Neural Network (ANN)-based model has been developed for the prediction of the hardness of arc melted and powder metallurgy route samples. A dataset of 16 samples has been utilized for the arc melted HEAs in which sensitivity analysis has also been reported due to less available dataset. While A particular class of HEAs by using 36 HEAs available data from the literature in case of powder metallurgy route HEAs. The model simulates the data by utilizing training, validation, and testing methods in a useful way. A backpropagation ANN has been used to predict the hardness value with an accuracy of 95.9% and 93.54% for powder metallurgy and arc melted HEAs, respectively. The developed model's predicted capability

also provides the freedom to choose the HEA composition with the required hardness of HEA without any experimental trials. Eventually, ANN has also been explored to understand the oxidation behavior of the proposed HEAs.

LIST OF PUBLICATIONS

List of published papers from this research work

- <u>Sheetal Kumar Dewangan</u>, Sumanta Samal, Vinod Kumar "Microstructure exploration and an artificial neural network approach for hardness prediction in AlCrFeMnNiWx High-Entropy Alloys" Journal of Alloys and Compounds, Volume 823,2020,153766, ISSN 0925-8388, <u>https://doi.org/10.1016/j.jallcom.2020.153766</u>. [SCI, IF: 4.65] (Chapter 3)
- <u>Sheetal Kumar Dewangan</u>, Sumanta Samal, Devesh Kumar, Vinod Kumar Microstructure and mechanical properties of nanocrystalline AlCrFeMnNiWx (X = 0, 0.05, 0.1, 0.5) high entropy alloys prepared by powder metallurgy route (Accepted in Journal of Materials Engineering and Performance, IF: 1.6) (Chapter 4)
- <u>Sheetal Kumar Dewangan</u>, Vinod Kumar Sharma, Priyanka Sahu, Vinod Kumar "Synthesis and characterization of hydrogenated novel AlCrFeMnNiW high entropy alloy," International Journal of Hydrogen Energy [Aug, 2019], https://doi.org/10.1016/j.ijhydene.2019.08.113. [SCI, IF: 4.939] (Chapter 5)
- Sheetal Kumar Dewangan, S. Samal, and V. Kumar, "Development of an ANN-based generalized model for hardness prediction of Spark plasma sintered AlCoCrCuFeMnNiW containing high entropy alloys," Mater. Today Commun. 27, 102356 (Elsevier Ltd, 2021). [SCI, IF: 2.67].

List of an ongoing manuscript from thesis work

- <u>Sheetal Kumar Dewangan</u>, and V. Kumar "Application of artificial neural network for prediction of the high-temperature oxidation behavior of AlCrFeMnNiWx (X = 0, 0.05, 0.1, 0.5) High Entropy Alloys" (submitted)
- 6. <u>Sheetal Kumar Dewangan</u>, S. Samal, and V. Kumar "A review on high-temperature applicability: a milestone for High Entropy Alloys" (under preparation)
- 7. <u>Sheetal Kumar Dewangan</u> and V. Kumar "Effect of heat treatment on processing route in AlCrFeMnNiWx High-Entropy Alloys" (under preparation)

Other Publications during Ph.D. period

- Ornov Maulik, Devesh Kumar, Saurav Kumar, <u>Sheetal Dewangan</u> and V. Kumar, Lightweight, high entropy alloys: A brief review, Materials Research Express, Vol 5, No. 5 (2018), <u>https://doi.org/10.1088/2053-1591/aabbca</u> [SCI, IF: 1.929]
- Priyanka Sahu; S. Solanki; <u>Sheetal Kumar Dewangan</u>; Vinod Kumar, Microstructure and Magnetic behavior of FeCoNi (Mn-Si)_x(x= 0.5,0.75,1.0) High Entropy Alloys, Journal of Materials Research, vol. 34, pp. 829-840, 2019. [SCI, IF: 1.982]
- Reliance Jain⁺, <u>Sheetal Kumar Dewangan⁺</u>, Sumanta Samal, Vinod Kumar, Artificial neural network approach for microhardness prediction of eight components FeCoNiCrMnVAINb eutectic high entropy alloys. Material Science & Engineering A, 2020, 140059, ISSN 0921-5093, <u>https://doi.org/10.1016/j.msea.2020.140059</u>. (SCI, IF: 4.5) {+ equal contribution}
- Jain R, Kumar S, Priyanka D, et al (2021), Microstructure Evolution and an ANN Approach for Microhardness Prediction of Suction Cast FeCoNiCrMnVNb Eutectic High-Entropy Alloys. Trans Indian Inst Met. https://doi.org/10.1007/s12666-021-02335-1

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LIST OF ABBREVIATIONS

- HEA High Entropy Alloy
- MA Mechanical Alloying
- SPS Spark Plasma Sintering
- XRD X-Ray Diffraction
- SEM Scanning Electron Microscopy
- BSE Back Scattered Electron
- EDS Energy Dispersive X-Ray Spectroscopy
- TEM Transmission Electron Microscopy
- STEM Scanning Transmission Electron Microscopy
- DSC Differential Scanning Calorimetry

Chapter 1

1.1 Background

Globally, the requirement of power is the primary necessity for livelihood. The generation of power mainly depends on the types of machinery and equipment used to produce the power, such as gas turbines and jet engines. The power generation industry mainly operates at high working temperatures, and the increased temperature helps to improve the overall efficiency of the industry [1]. The modern equipment is sophisticated, and high-strength materials are used to fabricate them. The high strength includes an outstanding specific strength, creep, and thermal resistance, not only at room temperature but also at high temperatures. Several studies provided a scientific way to design the equipment and its components for an improved life cycle in a critical working environment. Alike, the material also plays a vital role in developing an excellent design that meets the industry demands [2]. Since then, such material's requirement has brought a revolution in the field of materials science and engineering, and it originates from several discoveries from the last decades. Conventionally, it has one or two base elements, and more elements (alloying elements) are added to achieve the required properties.

The journey of pure metal to alloys and alloys to superalloys playing a crucial role in developing a new metallic material has been going on since ancient times. The development of civilization also grew simultaneously from the stone age to the bronze age to the iron age, and so on [3]. A schematic diagram represents the several age of development of the metallic material, shown in Fig. 1. The nickel-based superalloy having a monocrystalline structure is primarily known for its high-temperature strength and is widely used in turbine components [1]. The combinational effect of the precipitation hardening of ordered γ' particles and a substantial solid solution hardening of the γ matrix phase provides superior strength. The microstructure stability has been observed in the two-phase γ/γ' structure under several thermal and mechanical loading. The nickel-based superalloy has been investigated thoroughly, and a good understanding has been drawn in several reviews for high-temperature creep and fatigue behaviors [4–6]. Moreover, Mg-based alloys [7][8][9] and Al-based alloy have also been used as lightweight alloys, but they are not suitable for high-temperature applications.



Figure 1. 1 Development of material with increases in chemical complexity [10]

A new alloy class was developed by Cantor [11] and Yeh et al. in 2004, based on maximizing configuration entropy and forming a stable, single phase, substitutional solid solution [12]. The alloy consists of five or more than five elements with a concentration between 5 and 35 at %; therefore, it is also known as multi-component alloy, multi principal alloy, or complex concentration alloy [13]. The solid solution formation does not entirely depend upon the configuration entropy. At the same time, it has been seen in several studies that the formation of more than one phase and the compound is widespread. The single-phase solid solution formation has been seen in a particular range of compositions of alloying elements. It is worthy to note that enthalpy and non-configurational entropy have played an essential role in determining phase stability. However, configurational entropy has been observed as the primary driving force for the formation of a single-phase (as confirmed by the thermal analysis) [14][15]. The formation of the random solid solution could be influenced by various variable parameters like melting temperature, processing temperature, interatomic correlation, and properties of individual elements that are involved in the alloy system [10]. Fig. 1 describes the chemical complexity of different alloys by using a simple formula of ideal mixing entropy $(s_{id} = k_B \sum_{i=1}^{n} C_i lnC_i)$ in the vertical axis. The k_B is the Boltzmann constant, n is the number of the different elements, while C is used for the individual

elements' composition. It is worthy to note that proclaiming the enhancement of the properties in the case of the High Entropy Alloy (HEA) is also a function of the chemical complexity, which was seen in the several HEAs. The balanced combination of the high strength, ductility, and fracture resistance was seen in the HEAs [10].

Consequently, the unique multi-component alloy, including the equiatomic and non-equiatomic composition, has superior properties that are never seen in conventional alloys. Besides, this alloy's fabrication does not require any special process that is also attracting the new researcher to choose this as a research area. The high entropy alloy comprises the properties which have excellent mechanical properties [16][17] including hardness [18][19], wear resistance [20][21], strength [22][23], and structure [24] and thermal stability [25], magnetic properties [26–28] and corrosion resistance properties [29]. Apart from the mentioned properties, the alloy exhibits good high-temperature strength and high-temperature stability. The knowledge of phase structure makes it easy to acknowledge the mechanical properties as well as various unique properties associated with the HEAs. It has been seen that there is a significant improvement in the HEAs at different time scales as familiar with the phase structure. Recently, Chang et al. represented the expressive information on HEA development and explained phase engineering's correlation with the property enhancement on HEA from the last few years. A schematic illustration is given in Fig. 1. 2.



Figure 1.2 The roadmap of high entropy alloy with the enhancement of properties as the different timeline [30]

The knowledge of diffusion kinetics can better explain the understanding of several properties. The study of diffusion kinetics for the high entropy alloy at high temperatures has been very limited up till now. Thus, it is required to explore the diffusion experiment on HEAs. Tsai et al. [31] Performed a first-time diffusion experiment as a role of a diffusion barrier for copper metallization. In the experiment, it has been concluded that the Cu-AlMoNbSiTaTiVZr-Si sandwich structure prevented the inter-diffusion of Si and Cu at 750°C for 30 min.

Furthermore, it is suggested that the HEA can be used for the potential diffusion barrier for copper metallization. Tsai et al. [32] performed another diffusion study in 2013 in which FCC Co-Fe-Cr-Mn-Ni HEA has been utilized. A quasi-binary inter-diffusion coefficient was obtained at temperature range 1173-1333K, and the value is almost equal to the tracer diffusion coefficient. It is suggested that the diffusion coefficients are not sensitive to the composition of the diffusion couple, and it is smaller than the pure metal. The sequence of the diffusion rate in decreasing order was obtained as Mn>Cr>Fe>Co>Ni. A substantial amount of work has been done on diffusion in HEAs, and it will be detailed in a more specific way in the sluggish diffusion section.

Several review articles have been publishing in HEAs, and the courses of studies are mainly on room temperature properties. Hence, the focused review of high entropy alloy properties at high temperatures would benefit research communities working on HEA's application at high temperatures. The present assessment also conveys the brief facts of literature based on phase formation, microstructure evaluation, thermal stability, and different properties at high temperatures. The review also delivers a quick view of HEAs for a particular application based on their properties. Knowing the preparation method and different instruments for developing a high entropy alloy also provides new researchers guidelines. Eventually, the review would be handy for metallic material research communities to develop and understand HEA material properties at high temperatures.

1.2 High Entropy Alloys (HEAs)

1.2.1 Definition

High-entropy alloys constitute multi-principal elements (\geq 5), with each element has an atomic percentage of 5 to 35 [15-20]. Some studies suggest the definition must include that HEA must be a single-phase solid solution [21], and in others, the meaning is broadened to include four-component systems. There is no right or wrong answer, and the appropriate approach will depend

on the intent of the work being performed. Thus, there are multiple definitions of high entropy alloy based on composition, phase, etc., to allow researchers to explore the field with flexibility [22].

1.2.2 The concept behind HEA

The uniqueness of the HEAs is another identity in the field of metallic material. The alloy has several properties, mainly due to the significant core effects that make its properties exceptional. It is worthy to note that the core effects are also responsible for phases' strength and ductility, mainly due to solution hardening [33]. A brief understanding of the four-core effect has been discussed in this section.

1.2.2.1 The high entropy effects

The entropy mainly refers to configurational entropy, which is related to Gibb's free energy. As per the concept of high entropy, the entropy will be high, and hence free energy becomes low, leading to the stability of the phase. The enhancement in mutual solid solubility between the alloying elements and the number of phases presented in the HEAs could manifestly diminish. It could be appreciated by the Gibbs free energy equation, which is G = H-TS; here, G is the Gibbs free energy, H, S, and T belong to enthalpy, entropy, and temperature of the system, respectively. The entropy term will dominate if the temperature is sufficiently high, and high entropy will lead to a phase's stability. The entropy of metal would be high at melting state comparative to solid-state, and it could be said that the difference between two states is roughly equal to gas constant R by Richard's law [34][35].

Moreover, the phase with high entropy would probably be stable at a higher temperature. For example, as per the Gibbs phase rule [36], the possible number of phases would be six if the alloying components are 5. However, the high entropy alloy has a significantly less phase than predicted by the Gibbs law. The phenomenon could be explained by the existence of high mixing entropy in the HEAs. The high mixing entropy increases the solubility among the current phase in the given system, impeding the phase's possible separation to intermetallic phases.

The high entropy alloy has three possible states: elemental phases, intermetallic compounds, and solid solution phase. The elemental phase is based on one metal element, like one component, which could be on one side of the phase diagram. The intermetallic compound is like a stoichiometric compound, i.e., AlNi having a B2 structure, and it has a particular concentration

ratio in the phase diagram. The solid solution phase also has two categories: a random solid solution and an ordered solid solution. A random solid solution has been distributed with different components in a lattice site. It could be BCC, FCC, or maybe HCP, whereas the ordered solid solution is an intermetallic phase. However, the crystal structure could be based on the intermetallic compound, i.e., L1₂[34]. The stability of the HEAs' entropy is the fundamental design aspect, but it is also a challenge to design such HEAs. A few studies have reported that the HEA has a stable solid solution with all-temperature up to melting. Senkov et al. initially reported the BCC structured VNbMoTaW refractory high entropy alloy (RHEA), which is stable in all temperatures range up to melting [37]. A few years later, another RHEA was also reported by the same author, a TiV_xZrNbMo_y and a non-refractory Al_xCrFeCoNi HEA single-phase at less amount of x and y values. There is much evidence for the formation of a simple structure in HEA. The high entropy effect can be seen in several HEAs, i.e., NiFeCrCoMn [38] and CuNiAlCoCrFeSi HEAs.



Figure 1.3 XRD pattern of sequential addition of the elements from binary to septenary alloy
[34]

An example of CuNiAlCoCrFeSi HEA can explain the effect of alloying composition on phase formation. The alloy exhibited the BCC and FCC as a major phase from binary to septenary. However, it includes a small amount of intermetallic, which is not revealed in the XRD analysis

(Fig. 1.3). The formation of a simple phase also denies the conventional prospects of the formation of several phases. Thus the author also clears that the formation of simple solid solutions as a high entropy effect at high temperatures is not valid [34]. Besides, the increase in configurational entropy could stabilize the single-phase solid solution, which has also rarely been seen. The effect is insufficient to facet the formation of the secondary phase. The study also suggested that the single-phase solid solution by including more elements is also inadequate [14].

1.2.2.2 Sluggish diffusion effect

In the high entropy alloy, it has been seen that the diffusion in the HEAs is slow as compared to the conventional alloys. Diffusion becomes a crucial parameter while considering the high-temperature strength or high-temperature structure stability. Slowness in diffusion indicates a slower phase transformation or slower kinetics, which is a core effect in high entropy alloy. The sluggish diffusion in the HEAs case is very different from another alloy system because of the different arrangement of neighbor atoms. The atom's jumping into a vacancy brings a different neighbor to the lattice site. Due to the local atomic arrangement difference, the atoms have different bonds and different local energy for each site. Thus, when an atom jumps in the lower energy sites, it becomes trapped, and there are lesser chances to jump out.

On the other hand, if the jumping site is a higher energy site, there is a high probability of jumping back at its original site. In the other aspect, each constituent element has its diffusion rate. Some elements are highly active, and some have low activity depending upon their properties. So, the less active element has lower possibilities to achieve the vacancy by jumping [32] successfully. Unlikely in the conventional alloy, the circumstances are entirely different in the HEAs; thus, the kinetics of diffusion is sluggish. Moreover, researchers applied high entropy films to resist the diffusion due to their outstanding thermal and diffusion resistance [39].

Dabrowa et al. [40] experimented diffusion experiment on AlCoCrFeNi at a temperature range of 1273K-1373K. The results were compared with the CoCrFeMnNi HEA. It is found that there is a good connection between the literature data and experimental data, and it also confirms the theory of sluggish diffusion. Another research group, Kucza et al., performed extensive theoretical and experimental studies on quinary CoCrFeMnNi and quaternary CoCrFeNi and CoFeMnNi HEA. The quinary system's concentration profile was initially calculated and further utilized to estimate all elements' diffusibility by using a combination approach. A substantial qualitative agreement

has been seen in the radiotracer experiment's result. It is suggested that the diffusion kinetic does not affect the change in the number of components, and it does not support sluggish diffusion [41]. Recently, Esakkiraja et al. successfully demonstrated the newly adopted pseudo-binary and pseudo ternary method in the field of HEAs diffusion to observe the impact of alloying in the diffusion coefficient, which can be helpful to understand the various physical and mechanical properties. The method can be compared with the experimental data because the generated data set was involved with the combination of experimental and numerical analysis [42]. Jin et al. studied the inter-diffusion investigation in 7 diffusion couples with binary to quinary alloy. The study shows that NiCoFeCrPd HEA diffusivity is higher than NiCoFe and NiCoFeCr, which is unexpected and suggested that the HEA does not demonstrate the sluggish diffusion at absolute temperature. Moreover, the extrapolated diffusivities are lower against the pure and binary metals, but their values depend entirely on each specific constitutes [43].

In order to confirm the HEAs have sluggish diffusion, Kottke et al. compared the diffusion rates of elements presented in the HEA with the same system during the composition that may vary. In this work, the first-time volume diffusion has been measured in FCC single-phase solid solution HEA with composition $Cr_{10}Co_{10}Fe_{10}Mn_{10}Ni_{60}$, Cr₂Co₂Fe₂Mn₂Ni₉₂ and а а of Cr₂₀Co₂₀Fe₂₀Mn₂₀Ni₂₀ at 1373K. By keeping the same elements, the increase in the solute concentration does not promote sluggish diffusion. It has been found that in the homologous temperature scale, tracer diffusion of some constituent elements is found to be comparatively slower by one order of magnitude [44]. Recently, Dabrowa et al. performed another interdiffusion study on CoCrFeMnNi, CrFeMnNi, CoCrFeNi, and CoCrMnNi and a previous reported AlCoCrFeNi HEA. Initially, the diffusion couples are annealed at 1230, 1270, 1310, and 1350 K for each alloy. The optimization-based technique and Miedema's thermodynamic explanation have been employed to obtain the tracer diffusion coefficient. The approach was found in good agreement with the CoCrFeMnNi system. However, no sign was observed compared with the diffusivity values of conventional binary and ternary alloys in the absolute temperature scale. The study suggested that the sluggish diffusion in HEA on previously reported work is only a reason for the specific composition of individual elements. It could not be generalized for all high entropy alloys [45].

1.2.2.3 Lattice distortion effect

In multi-component alloys solid solution matrix, every atom is surrounded by another differently sized atom. Due to this atomic mismatch, the lattice suffers high strain and stress. The difference in atomic size is the leading cause of such lattice distortion. The existence of the different neighboring atoms, the different bonding energy, and the different crystal energy can also be the cause of lattice distortion. The unsymmetrical bonding and electronic structure can be seen unevenly in the lattice site [32]. Thus, it has been confirmed that the lattice distortion in HEAs is more severe than in the conventional alloy. It is also noted that the strain energy is related to the lattice distortion, which promotes the overall free energy of the HEA. Due to the phenomenon, the properties of HEA have been affected severely. The occurrence of solid solution strengthening is reasoned for the lattice distortion, which is mainly due to the hindering of dislocation movements. In addition, it also affects the electrical and thermal conductivity [34][46]. The atomic size difference is the major cause of the lattice distortion. Thus, an understanding of this parameter is essential. The lattice distortion primarily has two types: uniform lattice distortion and local lattice distortion [47]. In the uniform lattice distortion, the unit cell's expansion occurred uniformly to change the lattice parameters. Simultaneously, the systematic displacement from their actual position has been seen in the local lattice distortion [48]. The accurate prediction of the lattice distortion based on the specific rule's atomic radius is also doubtful [49]. A study also realized that the lattice distortion in HEAs is due to the charge transfer, not by the atomic mismatch [50]. However, some authors also investigated the physical scenario of an atomic size mismatch, and it will be useful for the complete understanding of HEAs [47]. Tong et al. investigated Pd's effect on local lattice distortion in a FeCoNiCr alloy and the Ni pure metal by the integrated approach of local structure characterization and Density function theory (DFT). The investigations have quantified the average local lattice distortion and fluctuation in the alloy. The experimental analysis revealed that the mean local lattice distortion value in FeCoNiCrPd was twice as NiPd. Whereas in the DFT calculation, the local lattice distortion has thoroughly related to the local lattice fluctuation in the FeCoNiCr matrix and proposed that the chemical complexity leads to an interactive effect in HEA [51].

The study of lattice distortion is not limited to experimental work; it has also attained several computation analysis milestones. The consequence of lattice distortion on HEAs' elasticity has been studied widely. Mainly molecular dynamics and molecular statics have been used for this purpose. Recently, Yen et al. have employed another model named Lennard-Jones to regulate the

strata of lattice distortion. In this study, the effect on young's modulus and Poisson ratio has been calculated in various directions. Finally, the work suggested that the Lennard-Jones model is insufficient to predict the elastic properties until the electron density consistency is not considered [52]. Wang et al. have experimented with evaluating the outcome of lattice distortion on the diffusion behavior of HEA via oxidation behavior. The works finding could be exploited to adapt to HEAs' diffusion and oxidation behavior by governing the lattice distortion [53].

1.2.2.4 Cocktail effect

In 2003, Ranganathan proposed for the first time for publication the "alloyed pleasures: multimetallic cocktails." The article suggested that the properties of the alloy are not limited to the properties of the individual elements. In contrast, the alloy shows composite properties due to mutual interactions between all the constituent elements. The composite properties also differ from the mixture rules, and they are unpredictable. The properties can be seen as wide, from an atomic scale to a micro-scale multiphase composite effect [54].

Further, yeh et al. present the work in 2006, which clearly demonstrated the cocktail effect. The experiment shows the Aluminum addition helps in the phase transformation from FCC to BCC in Al_xCoCrCuFeNi HEAs [55]. Moreover, the addition of Al also increases the hardness of the HEA while Al is soft and has a low melting point material. Afterward, Senkov et al. presented another example of a cocktail effect. The authors evaluated NbMoTaWV and VNbMoTaW refractory high entropy alloy with a melting temperature above 2600° C as per the rule of mixture. However, the alloy has more softening resistance than superalloys and shows high yield strength above 400MPa at 1600° C. The refractory alloy has excellent potential for high-temperature applications[37][56]. Other than these core effects, recently, yang et al. proposed a Local Atomic Configuration (LAC) as a core effect mainly due to the essential difference of local chemical configuration at the nanoscale [57].

1.3 Thermodynamic parameters for designing a HEA

A thermodynamic parameter plays a crucial role in designing a high entropy alloy. The discussed core effect could be related to some governing equations, and the governing equation is used to select the phase of HEAs. It is already known, the phase section is also directed by the Gibbs free energy G. The mixing of elemental composition during the alloy formation could be related to the

enthalpy of mixing Δ H_{mix} and entropy of mixing Δ S_{mix}. The relation between them can be formulated as equation (1.1) [58].

The competition between ΔH_{mix} and $T\Delta S_{mix}$ could determine the phase selection from different phases. The thermodynamic parameter, Ω , was previously proposed to define the mutual influence between ΔH_{mix} and ΔS_{mix} . Moreover, it recommends phase formation prediction whenever designing a multi-component alloy [59]. The parameter is described by the following relation[60].

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}....(1.2)$$

Where ΔH_{mix} is the enthalpy of mixing of binary alloys and $\Omega_{ij}(\Omega_{ij} = 4\Delta H_{mix}^{AB})$ is a parameter for the regular melt interaction between the *i*th and *j*th elements,

The entropy of mixing of n-elements is ΔS_{mix} . According to Boltazmen's hypotheses

$$\Delta S_{mix} = -R \sum_{i=1, i \neq j}^{n} (c_i \ln c_i)....(1.4)$$

Where C_i and R is the molar percent of the mixing elements and gas constant, respectively. The following relation can calculate the melting temperature T_m of the n element alloy where $(T_m)_i$ is the melting point of the ith element.

$$T_m = \sum_{i=1}^n c_i (\mathbf{T}_m)_i$$
.....(1.5)

The atomic size difference (\$) occurred due to the atomic difference between the pure metal. The parameter for the phase formation which is described through, and \overline{r} is the average atomic radius

of the alloying elements that the relation can calculate $\bar{r} = \sum_{i=1}^{n} c_i r_i$

The Valence electron concentration (VEC) is strictly connected to the phase formation; thus, it could be used as a quantitative prediction of phase, given by Guo et al.[61].

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i$$
.....(1.7)

Several experimental results have verified the validity of the mentioned rule, and the rules are widely used for the prediction of phases in the field of HEAs [30].

Very recently, Yang et al. performed an investigation on Al-Co-Cr-Fe-Ni HEA to verify the limitation of the VEC rules proposed by Gao et al. A careful examination of the manually generated VEC, VEC temperature phase diagram, and High Throughput Calculation of Equilibrium Solidification (TC-CES) was done. A set of randomly generated 41 compositions was calculated for VEC by Thermo-Calc, and phase transformation points are plotted in Fig. 1.4(a). This point is also utilized in the temperature-VEC plot shown in Fig. 1.4(b). The work suggested that the VEC parameter has a definite physical meaning for predicting the phase stability quantified, such as more than 90% of the investigated alloy has BCC if $5.7 \le \text{VEC} \le 7.2$ and 100% FCC structure when $\text{VEC} \ge 8.4$. It also provides the guideline for considering temperature and phase formation other than the solution phase, which helps design the HEAs [62].



Figure 1.4 (a) Phase transformation points and (b) VEC-temperature diagram of Al-Co-Cr-Fe-Mn HEA [62]

1.4 Processing routes for a HEA

The processing of the material to develop a high entropy alloy is not much different from conventional alloy. There are several ways to manufacture the HEAs in which the widely used

methods are casting, sputtering, splat quenching, and powder metallurgy[15]. Apart from these, High-pressure Torsion (HPT) has also been used to develop nanocrystalline materials, which have high strength and structure stability[24]. Commonly, the development of the HEAs has been classified into three categories, i.e., melting and solidification (Arc melting, die casting and induction melting), powder metallurgy (mechanical alloying and sintering), and deposition (plasma spraying, sputtering) [63]. The mentioned categories can be described in a further section.

1.4.1 Melting and solidification route

Classically, melting and solidification are extensively used for synthesizing the alloy. The melting and casting route has been used for the production of the HEAs since starting. The Vacuum Arc Melting (VAM) technique is the most favorable method[64], especially to achieve a high temperature. Since there is variation in the melting point of individual elements in the HEAs, the method worked for most metals. However, the most significant disadvantage of the method is the evaporation of the low boiling point metals; thus, it is difficult to maintain the compositional control in the HEA[65]. The melting and casting route has several advantages: less time consumption, cost-effectiveness, and energy-saving. Due to segregation at high temperatures, it has certain limitations, like dendrites and interdendritic formation [13]. The cooling rate during the solidification process has played a vital role in altering the microstructure and properties. The dendrites and volume fraction's growth in the interdendritic region and dispersion of the alloying elements could be seen in several works [66].

Interestingly, the effect of the cooling can also be observed in phase morphology and strengthening mechanisms [67]. In a study, the Al_xCoCrFeNi HEA was developed by two different routes: arc melting and suction casting method. The study clarifies that the high cooling rate in the suction casting method refines the microstructure and a change in phase morphology and strengthening mechanism. In Fig. 1.5 (a), a dendritic grain could be seen while producing via arc melting technique, whereas in Fig 1.5 (b), a non-equiaxed columnar dendrite grain is produced by suction casting [68].



Figure 1.5 Typical SEM image of Al_xCoCrFeMn HEA by (a) arc melted and (b) suction casting [68]

1.4.2 Powder metallurgy route

Powder metallurgy is the net shaping or near-net shaping manufacturing process, which combines the shape-making technology and design properties during the consolidating[69]. It is a solid-state powder processing technique involving repeated welding, fracturing, and powder particles' rewelding by the high-energy ball mill[70]. Mechanical alloying (MA) also involves the diffusion of species into one another to form a homogenous alloy. As a result, the formation of several advanced materials could be possible such as nanomaterial, intermetallic, quasicrystal, and amorphous[65], since the MA has several significant advantages as well as known for its versatility. The method is also useful for several hard, brittle materials and ductile metal alloys.

On the other hand, the method skips the numerous problems that occurred in the melting and solidification method. However, MA also has some disadvantages, mainly the contamination due to milling media. The problems of contamination could be reduced to some extent by proper selection of materials of balls, vail, and by use of high purity of inert gas [71]. It has been seen that the use of Process Control Agent (PCA) also involved unsolicited contamination during the milling process [72]. The reduced milling time could also be helpful to decrease contamination [73]. It is also worthy to note that the sequencing of the alloy can be made possible to reduce the contamination. Vaidhya et al. had a new approach to the sequencing of alloy. They introduced the individual elements step by step in a binary alloy during the mechanical alloying instead of the single step's conventional mixing of all elements. The nanocrystalline structure has been attained

in equiatomic AlCoCrFeNi HEA by mechanical alloying. It is interesting to note that, pure BCC phase has been achieved when the sequencing of the alloying was AlNi+Co+Fe+Cr, whereas 75% BCC and 25% FCC has been observed when the sequencing was FeNi+Co+Cr+Al [74].In a nutshell, the MA is an outstanding solid-state powder processing technique with various features; a brief view of their application has been presented schematically in Fig. 1.6.



Figure 1.6 An outline of the application area of mechanical alloying [75]

A fine-milled powder needs to be consolidated to form a bulk or dense pellet for further characterization. spark plasma sintering (SPS) is the widely used method for the consolidation of pulverized powder. There are several other methods used for the purpose like Vacuum Hot Pressing Sintering (VHPS) [76], Microwave sintering [77][78], and Hot Isostatic Pressing (HIP) [79].

The spark plasma sintering (SPS) is a novel, high-tech, and profitable technique to consolidate the powder and convert it into bulk material, which involves simultaneous heating and pressing the material. The SPS's unique features are the lesser holding time and lower operating temperatures compared to conventional methods such as casting and laser diffusion techniques. Short holding time and low temperature lead to lesser grain growth. Eventually, the spark plasma sintered product has obtained a better microstructure with an improved mechanical property [80]. It is frequently seen that the alloy made by MA followed by SPS has excellent mechanical properties as compared to VAM products. Kumar et al. showed differentiation in the material processing route. The investigation was involved with CoCrCuFeNiSi_x HEA synthesis by arc melting and

MA, followed by the SPs technique. There is the FCC + σ phase formation via SPS while only the FCC phase forms through VAM, which has increased the Si content to some extent. The study suggested that the spark plasma sintered sample exhibits better mechanical properties than the VAM sample, mainly due to the σ phase formation during the SPS process [81].

1.4.2.1 Hydrogen absorption capability

In this world, where the population is rapidly increasing day by day leads to an increase in energy requirements that demand clean and sustainable energy source/carrier. Hydrogen is considered a promising energy carrier due to fulfilling these energy demands, among all possible energy sources/carriers. Its favorable properties like abundant in nature, regenerative, environmentally friendly, etc. The only disadvantage of hydrogen is its low volumetric density that can be resolved by storing in cryogenic liquid form, compressed gas, or stored in solid materials. The solid form of storage of hydrogen in metal hydrides. Metal hydrides can be formed by exposure of alloy to the hydrogen flow. Among the three storage methods, solid form of storage is considered as most suitable and safe due to the advantages like (i) it prevents leakage because desorption occurs upon heat supply, (ii) heavy and bulky cylinders are not required, (iii) high energy investment not required, etc. unlike compressed gas and cryogenic liquid form of storage [82][83]

The photocatalysts water splitting system efficiently produces hydrogen by using solar energy [84]. The chemical reaction in which water is shattered down into hydrogen and oxygen. On the other hand, solar light-driven semiconductor heterostructures (HSs) are also a favorable green technique for hydrogen and prevention from environmental pollution. Since 1972, many attempts have been made to develop high efficient photocatalysts [85]. Nowadays, a researcher is looking for a balanced design of metal-free hierarchical nanostructure for next-generation photocatalytic systems [86].

Dong et al. [87] have synthesized Mg₃La alloy by ball milling and tested it for hydrogen absorption. The hydrogen storage capacity of 4 wt% is observed at 300°C, with the desorption capacity up to 2.7 wt%. It is also reported that the ball-milled Mg₃La alloy exhibits higher absorption capacity compared to cast Mg₃La at room temperature. A ball milling technique promotes the formation of a Nanocrystalline structure with Ni and can improve Mg-based alloy's absorption and desorption capacity [88]. Sanjay et al. [83] carried out experimental studies on the characterization of VTiCrAl alloy. The reaction enthalpies during absorption and desorption are
reported as 23 ± 4 kJ/mol and 34 ± 1 kJ/mol, respectively. The reaction kinetics are measured at 0°C, 20°C and 50°C and reported that the storage capacity is minimum at 50°C.

The maximum hydrogen storage capacity is found to be 1.0 wt%. On the other hand, Vinod and Anil [89][90][91] have carried out experimental studies on the measurement of hydrogen storage, reaction kinetics, and thermodynamic properties of different AB₅ materials like La_{0.9}Ce_{0.1}Ni₅, La_{0.8}Ce_{0.2}Ni₅, LaNi_{4.6}Al_{0.4}, and LaNi_{4.7}Al_{0.3}. It is reported that an increase in Ce content increases hydrogen storage capacity and decreases reaction enthalpy. In contrast, an increase in Al content decreases hydrogen storage capacity and increases reaction enthalpy. Swe kai Chen et al. [92] developed the C-14 Cr_uFe_vMn_wTi_xV_yZr_z high entropy alloy. An investigation for the hydrogen storage was performed through the result of the pressure- composition-isotherm and hydrogen absorption kinetics of the alloy. In this study, the effect of the change in lattice parameters before and after the absorption and desorption also been explored. Magnus moe et al. [93] investigate the hydrogen storage properties of Ti, Nb, Zr, Ta, and V based high entropy alloy and found that there is no correlation between the local strain and hydrogen storage capacity, while Zlotea et al. [94]proves that the absorption and desorption is a completely reversible process in the case of TiZrNbHfTa HEA which is an investigation by combining thermal analysis technique and in situ synchrotron. The rapid hydrogen absorption kinetic has been found in TiZrNbTa HEA at room temperature after a short incubation period, and the hydrogen mechanism determines by the nucleation and growth mechanism [95]. The VEC also plays an important role in hydrogen storage. It has been seen that destabilization of the metal hydride was due to the expansion of lattice, and it is tuned by altering the VEC [96].

A large number of metal hydrides have been studied for decades to identify their hydrogen storage capacity, but, unfortunately, most of the alloys are found incompatible for storage applications. For the metal hydrides based on transition metals, the storage capacity is limited to $H/M \le 2$. Apart from different studies on different types of metal hydrides, another approach of hydrogen sorption in alloys comes in to picture when Cantor et al. [11] have reported the microstructural studies on multi principal alloy and satisfy all the requirements of hydrogen storage [97]. The high entropy alloy, i.e., TiZrNbHf, is reported by Sahberg et al. [98] with an elevated hydrogen storage capacity of 2.5 wt%. The authors concluded that the lattice strain within the alloy is the reason behind higher storage capacity in both octahedral and tetrahedral interstitial.

Kunce et al. [99] have synthesized ZrTiVCrFeNi high entropy alloy using Laser Engineering Net Shaping (LENS) and optimized the LENS parameter to obtain better chemical homogeneity composition. The hydrogen storage experiments are performed at operating pressure and temperature of 100 bar at 50°C respectively and revealed the maximum hydrogen capacity of 1.81 wt%, whereas it is 1.56 wt% after annealing. The incomplete desorption was reported due to the presence of the C-14 hydride phase in the alloy. Zepon et al. [100] reported MgZrTiFeCoNi HEA with BCC structure produced by HEBM (High Energy Ball Milling) under Argon environment and storage capacity observed to be 1.2 wt%. It is also observed that during hydrogenation, the phase transition from BCC to FCC structure takes place as well, as the inverse phase transition occurs during dehydrogenation. Xiao et al. [101] suggested some non-equilibrium preparation methods improve the hydrogen storage properties of metal hydrides, such as mechanical milling, sputtering, and rapid quenching, which is successfully used for the AB5- type alloys.

1.4.3 Deposition route

Despite all methods, the coating of high entropy alloy is essential in the HEA processing route. However, the physical method like melting, casting, and mechanical alloying with rapid solidification is widely used to synthesize bulk materials [102]. Surface coating is an effective technique to improve the durability of structural components as well as resistance against the external environment, such as corrosion, wear, and high temperature. Since the HEAs have attractive properties for use as a coating material [103][104]. The HEAs are applied over the substrate surface in the form of a thick or thin layer to enhance the performance under suitable composition and deposition parameters. Recently, Le et al. [105] published an article on high entropy alloy-based coating and nicely described all aspects and processing routes. As per the literature, HEA-based coating has been divided into three primary categories that are HEA based metallic coating, HEA-based ceramic coating, and HEA-based composite coating. The HEAs have superior mechanical and functional properties, so research on the HEA base coating is also overgrowing. Thus, the study also describes a large number of the HEA-based coating synthesis route. The primary classification areas are (1) Laser/ plasma deposition[106], which includes laser cladding, laser surface alloying, plasma cladding, (2) Thermal spray[107, 108] in which Plasma

spray, high-velocity oxygen fuel spray, cold spray (3) Vapour deposition[109] comprises magnetron sputtering, the vacuum deposition.

Recently, Yin et al. [110] first time used the cold spray (CS) technique to produce FeCoCrNiMn HEA coating. The experiment proved that the solid-state cold spray has a potential method to develop a thick HEA coating with low porosity. Since the CS technique is a low-temperature process, it has been seen that no phase transformation has occurred. The CSed HEA coating is harder than the as-received HEA powder, mainly due to increased dislocation density and grain boundary. Wang et al. [111] synthesized the CoCrFeMnNi and (CoCrFeMnNi)₈₅Ti₁₅ HEA coating on the Q235 stainless steel substrate by plasma cladding. The BCC and FCC solid solution phase with the σ phase has been observed in (CoCrFeMnNi)₈₅Ti₁₅ HEA coating. It is six times harder than the CoCrFeMnNi HEA coating and exhibited better wear resistance at high temperatures.

1.5 High-temperature properties of HEAs

The modern industry demands a high-temperature strength material, which has excellent heat resistance and strength. In order to develop the high-temperature application material, several attempts have been made. In the last decades, numerous researchers involved in the invention of new materials for advanced applications. The nickel-based superalloys are one of them that exhibits excellent oxidation resistance and high-temperature strength. On the other hand, the major obstacle to meeting the high-temperature material demand is the high cost of the Ni-based superalloy [5]. Presently, the researcher is also looking to develop an alternative of these alloys by replacing the material, which lowers the production cost.

Commonly, the alloy has a base metal and added different elements to get desire properties in it. In contrast, a new class of alloys, which has no principal elements or every element, is a principal element. Thus it is called the multi principal or high entropy alloys (HEAs) [11][17]. The formation of high mixing entropy compared to intermetallic and metals is the reason for maintaining a severe random solid solution phase [112][78]. The high entropy alloys have unique combinations of the properties over conventional alloys, such as excellent strength [19], thermal stability, oxidation resistance [23, 113], and corrosion resistance [114, 115].

Interestingly, microstructure and properties are affected by different factors. In the high entropy alloys, four core effects play a very significant role in their feature. The four core effects are the

high entropy effect, sluggish diffusion, severe lattice distortion, and cocktail effect. The high entropy affects the thermodynamics of phase formation for the kinetics, while sluggish diffusion slows down the diffusion process. The severe lattice distortion affects the solid solution strengthen of the alloy while the cocktail effect brings excess to quantity predicted result by the mixture rule [116][59]. There are several conventional methods to processed high entropy alloys, such as vacuum arc melting (VAC), mechanical alloying (MA), Vapor deposition with sputtering, Plasma Spray, and most recently, powder metallurgy route followed by the spark plasma sintering (SPS). The processing route of the high entropy also greatly affected the alloys' properties [117][118].

Presently, most efforts have been expended to develop the HEAs, staying in critical environments such as high temperatures and hot corrosion atmosphere. The alloy should not only withstand these conditions but should also exhibit excellent mechanical behavior. Various engineering components are used at a high temperature. Due to the application at high temperatures, studying the material behavior at working temperature has been crucial. We also need to modify the material used for these applications for better performance as these components' performance depends on temperature. For example, for any heat engine, working capacity (i.e., the efficiency) increases with a rise in working temperature and similarly for jet engines [119]. Another positive aspect of high temperature is reducing fuel uses in various industries like nuclear, oil and gas industry etc. There are many more such high-temperature applications, and hence the high-temperature material is the need of the hour. Various Ni-based superalloys are being used for high-temperature applications. However, due to the melting point close to 1300 °C, the applications are limited to working temperatures in the range of 1160 and 1277 °C [1, 120]. Various properties of HEAs at high temperatures will be discussed in this thesis.

1.5.1 The HEAs resistance to oxidation

It is essential to inspect the oxidation behavior of various materials at higher working temperatures; materials tend to react and get oxidized and degrade their properties, which can be detrimental for the applications. Various studies have been performed on the oxidation behavior of HEAs. The resistance of the alloy AlSiTiCrFeCoNiMo_{0.5} and AlSiTiCrFeNiMo_{0.5} against oxidation was a crucial element in work done by Huang et al. [11], which mainly concentrated on the processing and microstructure of the alloys. The conclusion that was drawn out from the study was that the

reason for the excellent oxidation resistance of these materials lies in the presence of the chromium-based layer beneath the outermost titanium oxide scale.

Butler et al. examined the oxidation behavior of Al-Co-Cr-Ni-(Fe or Si) multi-component High-Entropy Alloys [121]. Arc Melting technique (raw materials with purity \geq 99.5%) was utilized to produce alloys. The alloy buttons with the composition of Al₁₀Cr_{22.5}Co_{22.5}Ni_{22.5}Fe_{22.5} (AL10F), Al₂₀Cr₂₅Co₂₅Ni₂₅Si₅ (AL20S), and Al₁₅Cr₁₀Co₃₅Ni₃₅Si₅ (AL15S) were manufactured on a watercooled copper hearth under an inert argon atmosphere. Each button was remelted with several ties to enhance uniformity. Oxidation tests (at constant temperature) were conducted in a normal room atmosphere at 1050 °C on as-cast specimens by varying the duration of tests from 1 hour to 1000 hours. X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM) were used to analyze the behavior. The formation of a discontinuous Cr₂O₃ scale was seen as a result of the oxidation of AL10F along with the presence of Al₂O₃ subscale, and AlN precipitates internally at 1050°C. The computation of mass increment during oxidation revealed that the AL10F HEA tends to follow a parabolic growth law. The continuous external Al₂O₃ scales containing a small volume fraction of Cr₂O₃ scale was seen to get thicker as the duration of oxidation increased.

Summarizing, oxide formation occurred via selective oxidation consistent with the oxide formation model devised by Giggins and Pettit for model Ni-Cr-Al alloys [122]. The variation in Al content displays changes in the product of oxidation. The lower Al content alloy formed an external. A Cr_2O_3 scale containing Al₂O₃ and AlN precipitates internally is formed at lower Al content. In contrast, the alloys with high Al content exhibited surface Al₂O₃ scales without any presence of other oxidation products.

Laplanche et al. studied the oxidation behavior of $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ High Entropy Alloy at 500-900 ⁰C in laboratory air (normal conditions) [123]. Induction melting was used to produce $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ in an alumina crucible from pure metals in elemental form (purity >99.9 wt %). The Thermogravimetric analysis (TGA) of the $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ HEA was done to study the oxidation kinetics. It revealed that the oxidation rate is initially linear and becomes parabolic in longer times. Beneath the oxide layer and over the surface of HEA, α -Mn₂O₃ with a thin Cr_2O_3 layer was observed at 600°C. The α -Mn₂O₃ transforms to Mn₃O₄ at 900°C after losing its stability

at 800°C. It was observed that Mn diffuses non-sluggishly in the HEA. The diffusion path provided to Mn in HEA due to pores' formation in the underlying CrMnFeCoNi substrate can decrease Mn's sluggish behavior.

Another investigation of the oxidation behavior of HEA was done by Gorr et al.[124]. The hightemperature oxidation behavior of Refractory high entropy alloy Nb₂₀Mo₂₀Cr₂₀Ti₂₀Al₂₀ at 900°C, 1000°C, and 1100°C was studied. The alloys were produced using the arc-melting technique in 0.6 atm of an argon atmosphere. The purities of the starting materials Mo, Nb, Al, Cr, Ti, and Si were more than 99%. A moderate mass increment was observed during the oxidation of refractory HEA. It was observed that at 900°C and 1000°C, the oxidation kinetics followed the linear rate law, while at 1100°C, the decelerating oxidation rate was observed after approximately 30h. As a result of the oxidation, the surface of HEA got covered by thick, porous, and non-protective oxide layers containing a mixture of various oxides. The addition of one atomic percent Silicon to the alloy Nb₂₀Mo₂₀Cr₂₀Ti₂₀Al₂₀ has resulted in a moderate improvement of oxidation behavior. The Si-free alloy has shown higher mass increment during oxidation than the Si-containing alloy. The experiment showed that though HEAs are a better choice for High-Temperature applications, their properties can be enhanced further by micro-and macro-alloying.

N. K. Adomako et al. investigated the high-temperature oxidation behavior of $Co_{33.3}Cr_{33.3}Ni_{33.3}$ (low-entropy alloy), $Co_{25}Cr_{25}Ni_{25}Mn_{25}$ (medium-entropy alloy), and $Co_{20}Cr_{20}Ni_{20}Mn_{20}Fe_{20}$ (highentropy alloy) [125]. These alloys were produced using plasma arc melting. For homogenization, the alloys were kept at 1000°C for 24 h and then cooled in the furnace. They were cold rolled to a 50% reduction, followed by annealing at 800°C for 2 h. Thermogravimetric analysis (TGA) was done to observe the mass change during the oxidation at various temperatures. These alloys followed a parabolic oxidation rate law in the temperature range of 800-1000°C. The oxidation resistance can be arranged as CoCrNi>CoCrNiMnFe>CoCrNiMn. The oxidation rate of CoCrNiMn increased due to Mn's addition because of the high diffusivity of Mn. The oxidation resistance was increased by the addition of Fe in CoCrNiMn. They decreased the Mn content, and the formation of more stable Cr_2O_3 was attributed to the observed increase in resistance against oxidation of CoCrNiMnFe. Shaik et al. examined CoCrCuFeNISix HEA's oxidation at 600, 700, and 800°C for 30h. Four different HEAs Co-Cr-Cu-Fe-Ni-Si_x (x=0, 0.3, 0.6, 0.9) with different Si content were produced [126]. The alloys were produced by spark plasma sintering (SPS) of a blended mixture of Co, Cr, Cu, Fe, Ni, and Si powders. It was concluded that up to 0.6 % Si content, the alloy's resistance against high-temperature oxidation increases, and after that, it starts to decrease. The oxidation rate kinetics study of alloys at the three designated test temperatures represented the typical cubic curve. Microstructural observation stated that the oxidation increased with an increase in the temperature.

1.5.2 The HEAs resistance to hot corrosion

Almost three percent of the world's total GDP is destroyed by corrosion. Various types of corrosion have been reported, and hot corrosion is one of them. It can be defined as the destruction of the passive oxide layer formed over material by the chemical interaction of some aggressive species like chlorides and sulfates. HEAs possess a unique microstructure, which can help resist corrosion. Studies have been done to see the effect of hot corrosion on HEAs like AlCoCrCu_{0.5}FeNiSi [127, 128], Al_xCrFe_{1.5}MnNi_{0.5}[114, 129], and Al_{0.5}CoCrCuFeNiB_x[130]. AlCoCrCu_{0.5}FeNiSi alloy was compared with SS 304 for corrosion behavior. Results stated that, at room temperature, AlCoCrCu_{0.5}FeNiSi alloy is more corrosion resistant than SS 304 in 1M H₂SO₄, but it displays bad pitting corrosion resistance than SS 304 in 1M H₂SO₄ and 1M NaCl. For Al_xCrFe_{1.5}MnNi_{0.5}, on decreasing Al content (i.e. decreasing x) corrosion resistance against 0.5M H₂SO₄ and 1M NaCl solutions increases. Al_{0.5}CoCrCuFeNiB_x alloys are more resistant to deaerated 1N H₂SO₄ than SS 304 and are not susceptible to localized corrosion.

Swe-Kai Chen has studied the effects of Al on Al_x (x=0,0.25, 0.50, and 1.00) CoCrFeNi HEAs in Sulphuric Acid [131]. Potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) were used to study corrosion. Tylczak et al. studied the corrosion behavior of HEAs CoCrFeNi₂ and CoCrFeNi₂Mo_{0.25} (referred to as A35 and A36, respectively) in 3.5 wt% sodium chloride (NaCl) at 25°C. Electrochemical methods were used in this study [132][122, 132]. Grain refinement affected their behavior as fine-grain in A35 increases weak spots for pits' initiation. On the other side, a protective layer along the grain boundary is formed in A36 alloy, contributing to its higher corrosion resistance. Potentiodynamic polarization results stated that in A35, alloy chloride ion got adsorbed on its surface, breaking the passive layer (the attack is localized in nature), resulting in pits' formation seen in microscopic analysis. The passivation is due to the formation of the Chromia layer. Nevertheless, chlorides' chemical attacks led to the oxide layer's breakdown and became vulnerable to pit formation. While in the case of alloy A36, no pitting was seen in microscopic analysis. This alloy passivates in the presence of NaCl solution and thus preventing pitting. Here also, Cr_2O_3 forms a passive oxide layer, but along with this, Mo stabilizes the oxide layer and enhances the alloy's corrosion resistance. The addition of Mo performed two functions in improving the corrosion resistance of A36 alloy-(a) helped form a more resistant layer against corrosion and (b) avoiding the advancement in pits' formation, hence decreasing pitting corrosion.

Li Ping et al. investigated hot corrosion behaviors of CoCrFeNiTi_{0.5} high entropy alloy in the mixture salt of Na₂SO₄-25%K₂SO₄ and Na₂SO₄-25%NaCl at 750°C[133]. CoCrFeNiTi_{0.5} displays relatively better hot corrosion resistance in Na₂SO₄-25%K₂SO₄ molten salts. The hot corrosion mechanism in Na₂SO₄-25%K₂SO₄ is based on preferential oxidation of Ti, Cr, basic fluxing of Cr₂O₃ in molten Na₂SO₄. The addition of NaCl to Na₂SO₄ accelerates the cracking and spalling of the oxide layer and promotes the formation of sulfides in corrosion-affected regions. The interaction of oxidation and chlorination dominates hot corrosion in Na₂SO₄-25% NaCl. Also, Fe's internal sulfidation contributes to the hot corrosion in both Na₂SO₄-25%K₂SO₄ and Na₂SO₄-25% NaCl salts. Zhao et al. reported Co content's effect on the corrosion behavior of Co_xCrCuFeMnNi HEA in a 3.5% NaCl solution [120]. The alloy was produced using vacuum hot pressing sintering. The electrochemical techniques involving the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used as an inspection tool to study the HEA's behavior in the given solution. It was observed that the corrosion resistance increased with the increase in Co content. The data obtained for $Co_{0.5}$ alloy were as: corrosion potential (E_{corr})= -964 mV, corrosion current density $(i_{corr}) = 4.04 \times 10^{-5}$ A cm⁻², and average corrosion rate $(V_{acr}) = 0.43$ mm year⁻¹. The EIS study revealed that the passive film formed over Co_xCrCuFeMnNi HEA becomes thicker and more resistive on increasing Co content. This depicts that the alloy with higher Co content showed better corrosion resistance.

1.5.3 Microstructural stability of materials

Microstructure plays an essential role in defining the mechanical properties of the alloys. Various mechanical properties like hardness, strength, toughness, ductility, oxidation behavior etc., depending on the microstructure. In HEAs, despite the presence of a multi-component system, the ultimate aim is to achieve a solid solution. Ni-based and Co-based superalloys have Υ and Υ'

phases in their microstructure, which gives them high-temperature strength. However, Ni-base superalloys are not stable at high temperatures due to the topologically close pack (TCP) phase formation, which is very detrimental and deteriorates the mechanical strength. HEAs have superior properties at high temperatures than superalloys, resulting from the sluggish diffusion effect and high entropy effect.

In the Al_{7.8}Co_{20.6}Cr_{12.2}Fe_{11.5}Ni_{40.7}Ti_{7.2} system, no TCP phases were observed after isothermal aging at 900°C for 300h. The mechanical properties were good while compared to the superalloys. The microstructure remained stable with Υ and Υ' phases after isothermal aging at 1050°C [134]. Lattice misfit parameter δ calculation also states about the microstructure stability at high temperature:

$$\delta = 2(\alpha \Upsilon' - \alpha \Upsilon) / (\alpha \Upsilon' + \alpha \Upsilon) \dots \dots \dots (8)$$

where α_{Υ} and α_{Υ} are the lattice parameters of Υ and Υ' phases, respectively. For Ni-based superalloy, the lattice misfit becomes more negative ($|\delta|$ increases) as the temperature increases. But for Al_{7.8}Co_{20.6}Cr_{12.2}Fe_{11.5}Ni_{40.7}Ti_{7.2} [134], Al_{10.3}Co₁₇Cr_{7.5}Fe₉Ni_{48.6}Ti_{5.8}Ta_{0.6}Mo_{0.8}W_{0.4} [134], and Al_{10.2}Co_{16.9}Cr_{7.4}Fe_{8.9}Ni_{47.9}Ti_{5.8}Mo_{0.9}Nb_{1.2}W_{0.4}Co_{0.4} [135], reduction in the misfit values ($|\delta|$) were observed with increase in temperature in the HEAs. Thus, it is responsible for better high-temperature properties of HEAs and their microstructure stability.

Lin et al. studied the microstructure stability of CrMnFeCoNiAl_{0.25} at 700°C [136]. The alloy's microstructure consisted of the FCC phase, which was not an equilibrium phase as it changed to the strip-like sigma phase (Cr-rich σ phase) and the B2 phase (NiAl). These phases precipitated from the FCC phase. Moreover, due to this up to 2000 h, the hardness and strength of HEA kept on increasing with increasing thermal exposure time. After 2000h, it was observed that the yield strength decreased with a further increase in the thermal exposure time due to the coarsening of σ and B2 phase (especially σ phase). Bala et al. investigated the effect of high temperature on the microstructure of Al₅Ti₅Co₃₅Ni₃₅Fe₂₀ HEA[137]. Followed by hot rolling and air-quenching, the alloy was heated to a temperature range of 650-900°C for 168h. The microstructure of hot rolled alloy consisted of Υ phase and was partially supersaturated. The air quenching leads to the formation of Υ ' phase was observed during high-temperature exposure. It was observed that at 700°C

and higher, additional continuous and discontinuous precipitation of Υ' occurred. After examining the alloy's final microstructure, it was revealed that it contained Υ and Υ' precipitates. The types of Υ' precipitates include spherical Υ' with bimodal distribution within the grains and the elongated DP γ' phases present at the grain boundaries. The alloy showed maximum mechanical strength after exposure to 650°C because of Υ' precipitation. Further increase in the temperature resulted in a decrease in mechanical properties.

1.5.4 Mechanical Properties at high temperature

The prime requirement for an industrial application, the mechanical properties at high temperatures, is an essential concern as the high-temperature studies are limited in HEAs. It has been observed that the effect of the temperature acts seriously on the strength of HEAs. However, high-temperature strength is a significant target during alloy design. In Fig 1.7, the specific strength has been plotted against the temperature, and it is compared with the conventional engineering alloys and various HEAs. Thus HEAs have the potential for high-temperature applications beyond the Ni-based superalloys[12].



Figure 1.7 The presentation of specific strength against the temperature of different HEA

The most commonly observed phenomenon is that with an increase in the temperature, the yield strength of metal decreases for superalloys consisting mainly of γ and γ' phases. However, the yield stress can increase abnormally with increasing temperature until it reaches about 800°C in

Ni-base superalloys, where the peak of flow stress is reached. For temperatures beyond 800°C, the yield stress decreases quickly [138] because γ ' starts rapidly dissolving.

A similar pattern was observed when Al₅Ti₅Co₃₅Ni₃₅Fe₂₀ [137] high-entropy alloy was studied. Even after hot rolling, the investigated alloy did not lead to supersaturation. After being hot rolled and air-quenched, the alloy was exposed to a 650–900°C temperature range for 168 h (7 days). When cooled air was applied, it led to precipitation of γ' . This precipitate was uniformly distributed within the microstructure. When the alloy was exposed to the high-temperature γ' particles grew in size. At 700°C and higher temperature, additional continuous precipitation (CP) and discontinuous precipitation (DP) of γ' was observed. The final microstructure of the alloy, when investigated, consisted of γ' matrix and γ' precipitates of three types. These were spherical γ' phases with bimodal distribution within the grains and elongated DP γ' phases present at the grain boundaries. Based on [139][140], it was concluded that there were γ' precipitates interspersed with the γ' matrix. γ' precipitates were additionally enriched in Ni, Co, Ti, and Al. Fe was located only in the γ' matrix.

The microstructure changes led to changes in alloy's mechanical properties with a temperature change. The influence of the exposure temperature on hardness, yield strength (YS), and ultimate tensile strength (UTS) was measured at 20°C and was presented in Fig. 1.8(a) and 1.8(b). the sample exposed to 650°C exhibited the highest hardness (455 HV10), and it exceeded the hardness in a hot-rolled state by 130 HV. No increase in the hardness was observed due to CP of γ ' after exposure to 700°C. Thus, the author has related this to γ ' precipitates growth prior to the microstructure after hot rolling and the beginning of the DP formation. The relationship can be seen. The hardness decreases to 350 and 260 HV after the exposure of samples to 800 and 900°C, respectively.



Figure 1.8 (a) Hardness (b) Engineering stress-strain curve for hot rolled and various hightemperature ranges [139]

A similar relationship was observed in tensile test results. After hot rolling, the material presented YS and UTS equal 775 MPa and 1045 MPa, respectively. Exposure to 650 and 700°C increased YS up to 1050 MPa and 990 MPa and UTS up to 1370 MPa and 1265 MPa, respectively. However, when exposed to higher temperatures, YS decreased to 490 MPa and UTS to 770 MPa like ordinary metals.

The authors have proposed the following scheme based on the Orowan bowing mechanism based on the above results. The high UTS in the case of samples exposed to 650 or 700°C has been related to slip band accumulation in the final step of tensile tests, which could be mainly on γ' precipitates. These precipitates were formed during cooling after hot rolling and have grown during high-temperature exposure. The γ' precipitates are responsible for strengthening nickelbased superalloys so that a dislocation can penetrate the field of γ' precipitates by either bypassing (the so-called Orowanbypassing mechanism) or cutting the precipitates. Eventually, the other illustrated their study as per the findings and best understanding, shown in Fig. 1.9.



Figure 1.9 Phase transformation pathway of the Al₅Ti₅Co₃₅Ni₃₅Fe₂₀ HEA [139]

The multimodal distribution of γ' allows superalloys to reach high yield strengths at temperatures even up to 750°C. While simultaneously maintaining high creep and fatigue life properties [138][141]. Kozar et al. [142] have proposed a model including multimodal γ' size effects by partially modifying the weak pair-coupling mechanism and introducing size distribution effects in the tertiary γ' superalloys, which are based on the same elements. When the secondary γ' particles are between 150 and 300 nm highest strength is achieved. Being exposed to 650°C led to growth in the size of γ' precipitates in the investigated alloy (between 50 and 200 nm), which results in the highest strength. After exposure to 800 and 900°C, the strength and hardness decrease due to continuing γ' particle growth (the ones precipitated during cooling after rolling), as dislocations no longer cut γ' particles but bypass them. The particles precipitated during exposure to 700°C were too small (less than 50 nm) to play an important role. The mechanical properties of the different HEAs at different temperatures have been given in Table 1.1.

| | | Mechanical Properties | | | | |
|---|------------------------|-----------------------|-------------|--------------------|------------------|------------|
| Alloy system | Phases | Т℃ | σy (MPa) | ε _p (%) | Hardness (HV) | Ref |
| C027.6Cr22.6Fe19.6Ni23.4Ta3.4Zr2.5 Al0.9 | FCC+ Laves phase | 800 | 659 | >50 | ~490- 642HV | [143] |
| AlCoCrFeNi _{2.1} | FCC + BCC | 750 | 1600 | 18 | 300-350 | [144] |
| AlCoCrFeNi _{2.1} | FCC + BCC | 25 | 1635±49 | 18±1.4 | - | [145] |
| C025.1Cr18.8Fe23.3Ni22.6Ta8.5Al1.7 | FCC+ Laves phase | 800 | 800 | 16 | | [146] |
| AlCoCrFeNi _{2.1} | FCC + BCC | 400 | 711 | | 278-316 | [147] |
| | | 600 | 676 | | | |
| | | 700 | 548 | | | |
| | | 800 | 309 | | | |
| $A_{10.3}NbTa_{0.8}Ti_{1.4}V_{0.2}Zr_{1.3}$ | BCC | 25 | 1965 | 5 | 500 | [148][149] |
| | | 800 | 678 | > 50 | | |
| | | 1000 | 166 | > 50 | | |
| Al _{0.3} NbTaTi _{1.4} Zr _{1.3} | BCC | 25 | 1965 | 5 | 490 | [148][149] |
| | | 800 | 362 | > 50 | | |
| | | 1000 | 236 | > 50 | | |
| Al _{0.4} Hf _{0.6} NbTaTiZr | | 25 | 1841 | 10 | 500 | [148][149] |
| | | 800 | 796 | >50 | | |
| | | 1000 | 298 | >50 | | |
| Al _{0.5} CoCrCuFeNi | FCC | 25 | 388 | | 210-300 | [150][149] |
| | | 300 | 411 | | | |
| | | 500 | 421 | | | |
| | | 700 | 426 | | | |
| | | 900 | 230 | | | |
| | | 1000 | 150 | | | |

Table 1.1 Mechanical property of HEAs at room temperature and high temperature

| | | 1100 | 80 | | | |
|---|----------|------|------|-----|---------|----------------|
| Al _{0.5} NbTa _{0.8} Ti _{1.5} V _{0.2} Zr | BCC | 25 | 2035 | 5 | 530 | [148][149] |
| | | 800 | 796 | >50 | | |
| | | 1000 | 220 | >50 | | |
| Al ₂ CoCrCuFeNi | BCC | 1000 | 116 | | 560 | [150] |
| | | 1100 | 79 | | | |
| | | 25 | 1620 | | | |
| | | 600 | 805 | | | |
| | | 500 | 1120 | | | |
| | | 700 | 567 | | | |
| | | 900 | 214 | | | |
| | | 800 | 302 | | | |
| AlCoCrCuFeNi | FCC+BCC | 25 | 948 | | 406-472 | [150][149] |
| | | 600 | 561 | | | |
| | | 700 | 307 | | | |
| | | 800 | 172 | | | |
| | | 900 | 98 | | | |
| | | 1000 | 47 | | | |
| AlCrMoNbTi | BCC | 400 | 1080 | 2 | | [151] |
| | | 600 | 1060 | 3 | | |
| | | 800 | 860 | 2 | | |
| | | 1000 | 594 | 15 | | |
| | | 1200 | 105 | 24 | | |
| AlMo _{0.5} NbTa _{0.5} TiZr | BCC | 25 | 2000 | 10 | 591 | [148][149] |
| | | 800 | 1597 | 11 | | |
| | | 1000 | 745 | >50 | | |
| | | 1200 | 250 | >50 | | |
| AlNb _{1.5} Ta _{0.5} Ti _{1.5} Zr _{0.5} | BCC | 25 | 1280 | 4 | 408 | [148][149] |
| | | 800 | 728 | >12 | | |
| | | 1000 | 403 | >50 | | |
| AlNbTiV | BCC | 25 | 1020 | 5 | 448 | [152] |
| | | 600 | 810 | 12 | | |
| | | 800 | 685 | 50 | | |
| | | 1000 | 158 | 50 | | |
| CrHfNbTiZr | BCC + Im | 25 | 1375 | 3 | 464 | [153][149] |
| | | 300 | 1420 | 4 | | |
| | | 500 | 1457 | 2 | | |
| | | 700 | 1322 | 1 | | |
| CrMo _{0.5} NbTa _{0.5} TiZr | BCC + Im | 25 | 1595 | 5 | 540 | [154][149] |
| | | 800 | 983 | 6 | | |
| | | 900 | 1328 | 5 | | |
| | | 1000 | 546 | 50 | | |
| | | 1200 | 170 | 50 | | |
| CrNbTiVZr | BCC + Im | 25 | 1298 | 3 | 482 | [155] [115] |

| 600 1230 10 800 615 >50 1000 259 >50 CrNbTiZr BCC + Im 25 1260 6 418 [1] 600 1035 >50 1 1 600 1035 >50 1 1000 115 >50 1 1000 115 >50 1 1000 115 >50 1 1000 115 >50 1 1000 814 30 1 11200 556 30 1 11200 556 30 1 11200 556 30 1 11200 187 50 1 11200 187 50 1 11200 187 50 1 11200 | | | | | 1 | | 1 |
|---|-----------------------------|----------|------|------|------|---------|----------------|
| $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ | | | 600 | 1230 | 10 | | |
| $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ | | | 800 | 615 | >50 | | |
| $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | | | 1000 | 259 | >50 | | |
| 600 1035 >50 1 800 300 >50 1 1000 115 >50 1 11000 115 >50 1 11000 115 >50 1 11000 115 250 1 11000 814 30 1 11000 814 30 1 11000 814 30 1 11000 814 30 1 11000 814 30 1 11000 556 30 1 11000 635 50 1 11000 635 50 1 11000 635 50 1 11000 635 30 1 11000 855 30 1 11000 855 30 1 11000 855 30 1 11000 855 30 1 11000 855 30 1 11000 855 30 1 11000 855 30 1 11000 240 50 1 11000 240 50 1 11000 240 50 1 11000 255 50 1 11000 1252 50 1 11000 1252 50 1 11000 235 50 1 11000 295 50 1 11000 295 50 1 | CrNbTiZr | BCC + Im | 25 | 1260 | 6 | 418 | [155][115] |
| 800 300 >50 HfMoNbTaTiZr BCC 25 1512 12 505 HfMoNbTaTiZr BCC 25 1512 12 505 1000 814 30 1000 814 30 1000 814 30 1000 814 30 11200 556 30 1000 635 50 1000 HfMoNbTiZr BCC 25 1575 9 1000 635 50 1000 HfMoTaTiZr BCC 25 1600 4 542 1000 1200 187 50 1000 1000 1000 1100 1000 <t< td=""><td></td><td></td><td>600</td><td>1035</td><td>>50</td><td></td><td></td></t<> | | | 600 | 1035 | >50 | | |
| Introduct Introduct <thintroduct< th=""> <thintroduct< th=""> <thi< td=""><td></td><td></td><td>800</td><td>300</td><td>>50</td><td></td><td></td></thi<></thintroduct<></thintroduct<> | | | 800 | 300 | >50 | | |
| HfMoNbTaTiZr BCC 25 1512 12 505 800 1007 23 1000 814 30 1000 1200 556 30 1000 814 30 1000 HfMoNbTiZr BCC 25 1575 9 1000 635 50 1000 HfMoNbTiZr BCC 25 1575 9 1000 635 50 1000 HfMoTaTiZr BCC 25 1600 4 542 1000 1000 855 30 1000 1000 855 30 100 | | | 1000 | 115 | >50 | | |
| 800 1007 23 100 1000 814 30 100 1200 556 30 100 HfMoNbTiZr BCC 25 1575 9 100 1000 635 50 100 1000 635 50 100 1000 635 50 100 4 542 100 <t< td=""><td>HfMoNbTaTiZr</td><td>BCC</td><td>25</td><td>1512</td><td>12</td><td>505</td><td>[156] [115]</td></t<> | HfMoNbTaTiZr | BCC | 25 | 1512 | 12 | 505 | [156] [115] |
| 1000 814 30 1000 1200 556 30 1000 HfMoNbTiZr BCC 25 1575 9 1000 1000 635 50 1000 635 50 1000 1000 635 50 1000 635 50 1000 1000 635 50 1000 635 50 1000 11000 635 50 1000 187 50 1000 11000 800 1045 19 1000 | | | 800 | 1007 | 23 | | |
| 1200 556 30 100 HfMoNbTiZr BCC 25 1575 9 1 1000 635 50 1 1 1000 635 50 1 1 11000 635 50 1 1 11000 635 50 1 1 11000 635 50 1 1 11000 187 50 1 1 11000 187 50 1 1 11000 800 1045 19 1 1 11000 855 30 1 1 1 1 11000 855 30 1 | | | 1000 | 814 | 30 | | |
| HfMoNbTiZr BCC 25 1575 9 MfMoNbTiZr 800 825 50 MfMoTaTiZr 1000 635 50 HfMoTaTiZr BCC 25 1600 4 542 HfMoTaTiZr BCC 1000 855 30 HfNbSi0.5TiV BCC + Im 25 1399 11 490 HfNbSi0.5TiVZr BCC 25 1540 17 464 HfNbSi0.5TiVZr BCC 25 1540 17 464 HfNbTaTiZr BCC 25 929 50 HfNbTaTiZr BCC 25 929 50 HfNbTaTi | | | 1200 | 556 | 30 | | |
| 800 825 50 100 1000 635 50 100 1100 187 50 100 1100 187 50 100 11100 1100 1100 1100 11100 1100 1100 1100 11100 1100 1100 1100 11100 111 1100 111 11100 111 111000 11100 11100 11100 111000 11100 11100 11100 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 111000 1110000 <t< td=""><td>HfMoNbTiZr</td><td>BCC</td><td>25</td><td>1575</td><td>9</td><td></td><td>[157] [115]</td></t<> | HfMoNbTiZr | BCC | 25 | 1575 | 9 | | [157] [115] |
| Image: state of the state | | | 800 | 825 | 50 | | |
| Image: Here in the state i | | | 1000 | 635 | 50 | | |
| HfMoTaTiZr BCC 25 1600 4 542 1000 800 1045 19 1000 1000 855 30 1000 11000 855 30 1000 11000 800 404 30 1000 11000 800 875 50 1000 11000 240 50 1000 1000 11000 240 50 1000 1000 11000 240 50 1000 1000 1000 11000 240 50 1000 1000 1000 1000 1000 11100 1000 240 50 10000 1000 1000 | | | 1200 | 187 | 50 | | |
| Image: second | HfMoTaTiZr | BCC | 25 | 1600 | 4 | 542 | [156] [115] |
| 1000 855 30 1000 1200 404 30 1000 11000 240 300 11000 11000 240 500 1000 1000 240 500 1000 11000 240 500 11000 11000 240 500 11000 11000 2400 500 11000 11000 2400 500 11000 11000 1252 500 11000 11000 1252 500 11000 11000 1252 500 11000 11000 1252 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 11000 295 500 11000 | | | 800 | 1045 | 19 | | |
| Image: here in the systemImage: here in the systemImage: here in the systemImage: here in the systemImage: here in the systemHfNbSi_{0.5}TiVBCCImage: here in the systemBCCImage: here in the systemImage: here in the systemImage: here in the systemHfNbSi_{0.5}TiVZrBCC25154017464HfNbSi_{0.5}TiVZrBCC25154017464HfNbSi_{0.5}TiVZrBCC25154017464HfNbTaTiZrBCC2592950295-390HfNbTaTiZrBCC2592950295-390Image: here in the system600675501m/doi:HfNbTaTiZrBCC1000295501m/doi:Image: here in the system11000295501m/doi:Image: here in the system11000295501m/doi:Image: here in the system11000790501m/doi: | | | 1000 | 855 | 30 | | |
| HfNbSi_{0.5}TiVBCC + Im25139911490 800 875 50 50 50 50 1000 240 50 50 50 50 HfNbSi_{0.5}TiVZrBCC 25 1540 17 464 600 1252 50 50 50 50 HfNbTaTiZrBCC 25 929 50 $295-390$ HfNbTaTiZrBCC 25 929 50 $295-390$ 1000 295 50 100 295 50 1000 295 50 100 295 50 11000 295 50 100 295 50 | | | 1200 | 404 | 30 | | |
| 800 875 50 100 1000 240 50 100 HfNbSi0.5TiVZr BCC 25 1540 17 464 600 1252 50 100 100 100 100 HfNbTaTiZr BCC 25 929 50 295-390 100 HfNbTaTiZr BCC 25 929 50 295-390 100 11000 295 50 100 100 295 50 100 11000 295 50 10 10 | HfNbSi _{0.5} TiV | BCC + Im | 25 | 1399 | 11 | 490 | [158] [115] |
| 1000 240 50 1 HfNbSi0.5TiVZr BCC 25 1540 17 464 600 1252 50 1 1 1 1 HfNbTaTiZr BCC 25 929 50 295-390 1 HfNbTaTiZr BCC 25 929 50 295-390 1 1000 295 50 1 1 1 1 1100 295 50 1 1 1 1 11000 295 50 1 1 1 1 11000 295 50 1 | | | 800 | 875 | 50 | | |
| HfNbSi0.5TiVZrBCC25154017464600125250600125250HfNbTaTiZrBCC2592950295-390600675506005355010002955012009250 | | | 1000 | 240 | 50 | | |
| 600 1252 50 1 800 427 50 1 HfNbTaTiZr BCC 25 929 50 295-390 600 675 50 1 1 1000 295 50 1 1 11200 92 50 1 1 11400 790 50 1 1 | HfNbSi _{0.5} TiVZr | BCC | 25 | 1540 | 17 | 464 | [159] [115] |
| 800 427 50 50 HfNbTaTiZr BCC 25 929 50 295-390 600 675 50 50 50 50 1000 295 50 50 50 50 1000 295 50 50 50 50 11000 295 50 50 50 50 11000 1200 92 50 50 50 | | | 600 | 1252 | 50 | | |
| HfNbTaTiZrBCC2592950295-39060067550501001008005355010010010002955010010012009250100100 | | | 800 | 427 | 50 | | |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | HfNbTaTiZr | BCC | 25 | 929 | 50 | 295-390 | [160] [115] |
| 800 535 50 1000 295 50 1200 92 50 1400 790 50 | | | 600 | 675 | 50 | | |
| 1000 295 50 1200 92 50 1400 790 50 | | | 800 | 535 | 50 | | |
| 1200 92 50 1400 790 50 | | | 1000 | 295 | 50 | | |
| 1400 790 50 | | | 1200 | 92 | 50 | | |
| 1.00 ,,,0 | | | 1400 | 790 | 50 | | [161] |
| HfNbTaTiZrW BCC 25 138 26.3 - | HfNbTaTiZrW | BCC | 25 | 138 | 26.3 | - | |
| 800 52 >35 | | | 800 | 52 | >35 | | |
| 1000 37 >35 | | | 1000 | 37 | >35 | | |
| 1200 31 >35 | | | 1200 | 31 | >35 | | |
| HfNbTaTiZrMoW BCC 25 1637 15.5 - | HfNbTaTiZrMoW | BCC | 25 | 1637 | 15.5 | - | [161] |
| | | | 800 | 1065 | >35 | | |
| 800 1065 >35 | | | 1000 | 736 | >35 | | |
| 800 1065 >35 1000 736 >35 | | | | | | | |

1.6 Advanced high entropy alloy for high-temperature applications

1.6.1 Refractory high entropy alloys (RHEA)

The requirement of materials for high-temperature applications has always been a crucial need. Many materials like Ni-based superalloys have been used for the same purpose. However, their limitation in thermal stability and melting point (1300°C) has led to novel materials development. The concept of high entropy alloys (HEAs) was introduced by Yeh et al. [162] and Cantor et al.[11] independently. Based on the same idea, Senkov et al.[37] proposed the concept of refractory high entropy alloys (RHEAs) composed of refractory elements and hence exhibited a too high melting point. They show an exceptional combination of high hardness and strength, excellent oxidation resistance, and excellent resistance to wear and corrosion. These properties at high temperatures are required in various applications like aerospace, jet engines.

These excellent combinations of high-temperature properties have attracted the attention of many researchers. Various studies have been proposed regarding the stability, microstructure, mechanical properties, corrosion, and oxidation behavior of RHEAs



Figure 1.10 XRD pattern for 40h mechanically alloyed powder [163]

Microstructural stability is very crucial for the RHEA at higher temperatures to offer exceptional properties. The stability of a nanocrystalline MoNbTaTiV refractory high entropy alloy at high temperatures has been studied by Wang et al. [163]. The alloy was prepared by mechanical alloying. XRD and SEM analysis were utilized to study the phases present and grain size as a function of milling time (0 hours to 40 hours). XRD (Fig 1.10) shows an amalgamation of all the elements into a BCC phase at 20 hours, as the peaks related to the elements disappeared at 20 hours. SEM analysis depicted that the lamellar spacing and holes present in the alloy decreased with increased milling time. Annealing treatment estimated the thermal stability of the alloy. The nanoscale grain size and bcc phase were maintained after the annealing treatment at 800°C to 1200°C. These represent the excellent thermal stability of the MoNbTaTiV RHEA at high temperatures.

In another study done by Yao et al. [164], the phase stability of a single ductile phase BCC $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA at various temperatures has been reported. The alloy was prepared by suction casting, and its structure was single-phase, having a BCC structure. To investigate thermal stability of phases, annealing (for 14 days) at various temperatures 500, 700, 800, and 900°C was done. At 900°C, the bcc phase remains stable. Examining samples at 800°C revealed tiny second phase particles at grain boundaries (GBs), and the RHEA had a single-phase structure similar to that in 900°C. After annealing at 800°C, the SEM analysis showed NbTa rich precipitates (having BCC structure) mainly on the GBs and in some intragranular regions. After annealing at 500°C, a three-phase microstructure was observed. Those phases include an HCP phase enriched with Ti, a BCC1 phase enriched with Hf and Zr, and a BCC2 phase in Nb and Ta. This study showed the phase stability of $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA, and it is seen that the RHEA is stable at high temperatures and does not disintegrate in other phases.



Figure 1.11 Presentation of strain-stress curves at room temperature (RT), 800°C, 1000°C, and 1200°C of (a) H-W; (b) H-MoW alloys and (c) comparative study of yield strengths of both alloys at RT, 800°C, 1000°C, and 1200°C [161]

Investigating mechanical properties at high temperatures is crucial as it defines how the material will behave under operational stress and, ultimately, its performance at high temperatures. In the study done by Yao et al. [164], the stability was discussed for the HfNbTaTiZr refractory high entropy alloy. Moreover, Wang et al.[161] reported the effects of W and Mo-W in addition to equimolar HfNbTaTiZr RHEA. The microstructure showed the presence of two disordered bcc phases in HfNbTaTiZrW (H-W) and HfNbTaTiZrMoW (H-MoW) alloys in contrast to a single bcc phase in HfNbTaTiZr (H) alloy. The HfNbTaTiZrW and HfNbTaTiZrMoW alloys exhibited improved yield strength at 25-1200°C compared with HfNbTaTiZr. The value recorded for the yield strength of HfNbTaTiZrW and HfNbTaTiZrMoW alloys at 1200°C is 345 MPa and 703 MPa, respectively, which is much higher than 92 MPa of HfNbTaTiZr alloy (Table 1.1). The stress-strain graphs obtained for RHEAs are shown in Fig 1.11 [161].

The high strength of HfNbTaTiZr -W, and HfNbTaTiZr -MoW alloys resulted from dual-phase microstructure, and solid solution strengthening occurred due to the addition of W and Mo. Also, it was reported that no generation of new phases was seen in the RHEAs during high temperatures compressions up to 1200°C, which indicates the superior thermal stability of the RHEAs. The ductility of RHEA at various working temperatures is of great concern. RHEA shows high yield strength and high melting point, but their industrial applications are restricted due to their limited ductility. Regarding this, a study was done by Guo et al. to observe the effectiveness of powder metallurgy in preparing a ductile NbTaTiV RHEA [165]. It was reported that the RHEA prepared

through this route exhibits excellent ductility at room temperature as well as at higher temperatures. A good combination of high yield strength (437 MPa) and more than 40% compression strain was observed at 1000°C. Such high strength can be designated to homogenous and fine microstructure obtained with powder metallurgy and solid solution strengthening. Thus, a conclusion can be drawn that the RHEAs have excellent high-temperature mechanical properties, and also, their microstructure is thermally stable at high temperatures.



Figure 1.12 Mechanical properties of MoNbTaTiVAl_x at (a) room temperature (b) 500° C (c) 700° C (d) 900° C [166]

To further improve RHEA properties, various strategies related to different alloying metals are being proposed. Under these considerations, Al addition has been vastly studied as it reduces the density of the alloy as well as promotes order in the system. Shaofan et al. studied Al alloying's effects on the mechanical properties of MoNbTaTiV RHEA [166]. The RHEAs with nominal compositions of Al_xMoNbTaTiV (x = 0, 0.2, 0.4, 0.6, 1), are designated as Al0, Al0.2, Al0.4, Al0.6, Al1, respectively. These were prepared using a vacuum arc melting technique. Fig. 1.12 represents the stress-strain curve for different alloy compositions at room temperature, 500, 700, and 900°C. Table 1.2 depicts the experimental values of yield stress (σ_y) and compression strength (σ_p) of the RHEAs. The observed microstructures of all the alloys are of dendritic structure. It is concluded that with the addition of Al, the yield strength of alloys is increasing, as shown in Fig. 1.13. An increment in yield strength was observed from 1228 MPa to 1391 MPa, and in the hardness from 421 HV to 575 HV. These mechanical properties improvement is based on solid solution strengthening, which depends on chemical and electronic interactions. This study shows the idea of alloying RHEA with other metals and how the result leads to improve properties.



Figure 1.13 Yield strength Hardness, lattice parameter of Al_xMoNbTaTiV (x = 0, 0.2, 0.4, 0.6, 1) HEAs [166]

Table 1.2 Mechanical properties of MoNbTaTiVAlx (a)0, (b)0.2, (c)0.4, (d)0.6, (e)1 [166].

| X | Hv | σ _{0.2} (MPa) | σ _p (MPa) |
|-----|-----------|------------------------|----------------------|
| 0 | 421.7±7.9 | 1227.9 | 2066 |
| 0.2 | 473.6±9.2 | 1292.0 | 1791 |
| 0.4 | 510.0±8.5 | 1332.2 | 176 |
| 0.6 | 532.0±7.7 | 1352.9 | 1868 |
| 1 | 574.8±9.6 | 1391.2 | 1436 |
| | | | |

Various marine applications, naval applications, and chemical vessels like gas or any fluid pipelines require excellent corrosion resistance in the material used. The refractory high entropy alloys are used in such applications, and hence it is crucial to examine the corrosion behavior of RHEA. In the study done by Zhou et al., the corrosion behavior of $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA in aqueous chloride solution was examined [167]. $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA has a single-phase bcc in its microstructure with equiaxed grains of size 160 µm. It was concluded that the RHEA exhibited excellent corrosion resistance confirmed by lower corrosion current density and high pitting potential (+8.36 V). HEA's alloying concept ensured the homogenous distribution of high content of Hf, Nb, Ta, Ti, and Zr in a single-phase solid solution, which promotes passivity. The corrosion resistance of the RHEA was enhanced due to the presence of metallic Ta and ionic OH⁻ species. This shows that the RHEA exhibits excellent corrosion resistance properties.

As RHEA is used at high temperatures, it is essential to study alloy's oxidation behavior. Zhang et al. reported the change in NbZrTiCrAl refractory high entropy alloy properties at 800°C, 1000°C, and 1200°C for 50 hours due to the oxidation process[168]. The oxidation kinetic curve is shown in Fig 1.14. The kinetics curve for oxidation at 800°C shows a slow mass increment of the alloy during oxidation. For oxidation at 1000°C, in the initial 25 hours, the mass change increases slowly, but after that, it increases a little bit faster. While oxidation at 1200°C showed a sharp mass increase of the alloy. The mass gain behavior of the alloys at these temperatures follows the Power law.

$$\Delta m = kt^n \dots (9)$$

Where Δm is mass gain per unit surface area (mg cm⁻²), t is the holding time (h), k is the oxidation rate constant (mg cm⁻² h⁻¹), and n is the time exponent).

For oxidation at 800 and 1000°C, n values are estimated to be 0.57 and 0.64, respectively, and at 1200°C estimated n value is close to 1. These n values provide information about oxidation kinetics. The oxidation process follows parabolic oxidation kinetics at 800°C and 1000°C, and at 1200°C, oxidation obeys linear kinetics. The oxide layer formed at higher temperatures contains mainly CrNbO₄ and some ZrO₂, TiO₂, and ZrNb₂O₇. The layer is dense and homogenous for oxidation at 800°C and 1000°C, while for 1200°C, the layer possesses porosity and layered structure. It has been concluded that the alloy exhibits good oxidation resistance at 800°C and 1000°C and 1000°C but degrades after that and exhibits poor oxidation resistance at 1200°C. It can be seen in Fig. 1.14 that mass gain is high for oxidation at 1200°C than that at 800°C and 1000°C.



Figure 1.14 Oxidation kinetic curves of the NbZrTiCrAl alloy oxidized at 800°C, 1000°C, and 1200°C, respectively [168].

Concluding the various studies, the refractory high entropy alloy (RHEA) exhibits excellent hightemperature properties, be it stability, corrosion resistance, or strength. Hence these materials can be beneficial in the industrial sector as they would enhance efficiency and provides a path for further research in this area.

1.6.2 Eutectic high entropy alloys (EHEA)

Single-phase FCC HEAs are not had enough strength but have ductility, while bcc single-phase HEAs can be good but have limited ductility [169] [170]. In HEAs, castability and compositional segregation are common problems that reduce their mechanical properties [171][150]. Eutectic or near-eutectic high entropy (EHEA) alloys are a class of HEAs, which consist of one hard laves/TCP/intermetallic another ductile solid solution with lamellar and phase morphology[172][173][174]. The dual-phase in EHEAs provides good thermal stability and high temperature softening, making the EHEAs a favorable candidate for high-temperature application[175][176]. Therefore, attempts have been made to understand hot-workability (mechanical properties at high temperatures). Sumanth et al. [9][177] proposed the equiatomic CoCuFeNiTi EHEA having BCC (β) and FCC (α_2) solid solution phase and eutectic between FCC (α_2) and Ti₂(Ni, Co)-type Laves phase. They found optimum hot workability conditions in the temperature range from 930°C to 990°C (1203 K-1263 K) and strain rate in the range of 10^{-3} s⁻¹ –

10⁻¹ s-1. Reliance et al.[178] reported hot workability of Co-Fe-Mn-Ni-Ti EHEAs at temperature range 800°C-1000°C and different strain rate (10⁻³,10⁻²,10⁻¹and 1 s⁻¹), Co-Fe-Mn-Ni-Ti EHEAs consist of FCC CoFeNi-rich (α) and bcc Ti-rich (β) solid solution and eutectic between fcc CoFeNi-rich (α) and Ti₂(Ni, Co) type Laves phase. They found the optimal hot workability condition in the temperature range 800°C -1000°C and strain rate range 10⁻³ s⁻¹-10^{-1.6} s⁻¹ as well as 857°C -952°C and strain rate10^{-0.5}-1 s⁻¹. Furthermore, the AlCoCrFeNi_{2.1} EHEA having two alternating fcc and bcc lamella showed good fracture strength and plastic strain at room temperature and elevated temperature. AlCoCrFeNi_{2.1} EHEA showed the 944 MPa fracture strength and 25.6 % plastic strain under tension at room temperature and further the yield stress, fracture strength, and elongation were 95 MPa, 806 MPa, 33.7% at 600°C and 108 MPa, 538 MPa, and 22.9% at 700°C, respectively [172]. Further, AlCoCrFeNi_{2.1} EHEA has better strength as compared to known high-temperature NiAl-based eutectic alloys at least up to 700°C. The AlCoCrFeNi_{2.1} EHEA shows a lower density (7.38 g/cm³) over Ni-based superalloys (8.0 g/cm³) [172][179]. Finally, EHEA with low density will be competing with the Ni-base superalloys for high-temperature applications.

1.6.3 High entropy superalloys (HESA)

Conventionally, the Ni-based superalloy has played an essential role for the last six decades consistently. The Ni-based superalloy has been used to improve gas turbines' operating temperature, further used in air transport and power generators to reduce emission and fuel consumption [180]. It has excellent high-temperature mechanical and physical properties; thus, the alloy is widely used for the automobile, aerospace, and energy sectors. Nevertheless, researchers explore a new class of high-temperature alloys to replace the existing Ni-based superalloys. A novel alloy was discovered called AlCoCrFeNiTi based high entropy superalloy (HESA) by yeh et al. [181]. Interestingly, it has been observed that the compositional space of HESAs is so far from the conventional Ni-based superalloys and equimolar HEAs, as can be seen in Fig. 1.15(a). Furthermore, by using the same concept, Sao et al. designed HESA (HESA-3)[135], which has an FCC matrix with L1₂ ordered precipitates. Besides, the creep resistance of the HESA was comparable with the Ni-based superalloys. Experimentally, it has been observed that the HESA has the main strength due to low stacking fault energy, high anti-phase boundary energy, and thermal stability microstructure. The HEA has been proposed as a new category of HESA that

reduced the cost-effectiveness compared to conventional Ni-based superalloy. The comparison of the HESA with the CM247LC superalloy is shown in Fig. 1.15(b).



Figure 1.15 Schematic presentation of (a) Alloy design space for high entropy superalloys, and (b) comparison of properties and performance of HESA-3 [182] [135] and CM247LC

Moreover, the HESA has a similar microstructure as conventional Ni-based superalloy possesses FCC- Υ matrix with the L1₂- Υ' precipitates. Additionally, the four core effects also have been utilized to develop the HESA. While a few refractory elements have been used, lighter HESAs have been developed compared to Ni-based superalloy. Evidently, Fig. 1.16 (a) presented Υ' particles over Υ matrix, while superlattice reflection was shown in Fig. 1.16 (b).



Figure 1.16 TEM analysis of HESA (a) dark-field image, (b) diffraction pattern. [181]

Another superalloy class was reported by Senkov et al. in 2016, in which the refractory element has been employed [148][183]. The RHESA AlMo_{0.5}NbTa_{0.5}TiZr has two phases that have decomposed from the BCC phase. It consists of ordered B2 and disordered BCC coherent phases leading to high-temperature stability and high specific strength. It is reported that the alloy's high strength is due to mixtures of two phases (order and disordered crystal structure) in nanoscaled, and it restricted the deformation flow. Thus, the high thermal stability of the RHESA holds its high strength at high temperatures, even up to 1200°C. Comparably, an illustration has been presented in Fig. 1.17 in which the RHESA achieved higher yield and specific yield strength than those of the conventional Ni-based superalloy in the temperature scale from 20 to 1200°C [183].



Figure 1.17 The illustration of (a) yield strength and (b) specific yield strength against the temperature of the RHEA superalloy AlMo0.5NbTa0.5TiZr [183].

Recently, the effect of Al contents in Al_xTaTiZr RHESA has been evaluated [184]. Experimentally, after extended exposure for 1000 hr at different high temperatures, the alloy developed a nanoscale weave microstructure. The alloy has the BCC phase and ordered B2 phase in those of the Al contents less than 5 (at.%). Moreover, the ordered phase was only stable up to 900°C means the ordered phase did not provide strength at a high temperature of more than 900°C. However, newly found that a minor amount of Nb could advance the oxidation resistance of Al_{0.2}Co_{1.5}CrFeNi0_{1.5}Ti_{0.3} HESA [185]. The Nb (0.9 at.%) added HESA has present 40% less weight gain and oxidation resistance enhanced by 66% against those of the higher Nb content HESA. At the same time, the tensile property has also been slightly enhanced. Apart from the

conventional casting method of developing HESA, Kang et al. produced $Ni_{46}Co_{22}Al_{12}Cr_8Fe_8Ti_3Mo_1$ HESA via powder metallurgy in which high energy has been employed, followed by SPS. The HESA achieved Υ ' precipitates within the FCC matrix, which provides high yield strength by limiting the dislocation movement. The authors reported outstanding yield strength of 1355 MPa while ductility of 8.7% [186].

In this chapter, I review the previous studies of HEAs. As per the findings of this literature review, the achievements of previous findings are summarized the objectives of the research are clarified as well.

In order to achieve the goal, the following methodology has been adopted, which is shown in Fig. 1.18. The next chapter will discuss the materials and experimental details to fulfill the methodology discussed in Fig. 1.18.



Figure 1.18 Flow diagram showing methodology for development and characterization of HEAs

1.7 Objectives of the Research Work

The demand for high strength, superior corrosion resistance, and application in high-temperature materials is increasingly becoming a requirement for better energy efficiency in structural and marine applications. Some of the conventional alloys like Al-based and Mg-based have poor mechanical properties compared to steel and are also not suitable for high-temperature applications. High-strength alloys like refractory alloys (base alloy) are not cost-effective. The shortcomings and requirements motivated the investigator to research to synthesize high entropy alloys (HEAs) to achieve properties such as higher strength to weight ratio, excellent mechanical properties such as hardness, and superior corrosion resistance similar to stainless steel.

Still, there are major complications in designing high-strength HEAs. Most of the periodic table elements possessing high strength and high melting point have high density and low ductility. Also, most of these elements are immiscible with the transition group of elements in the periodic table due to their varying atomic radius and high positive enthalpy. Also, many refractory HEAs made of high-melting transient metal elements such as Ta, W, Nb, Mo, and V exhibit high strength and low plasticity. Tungsten is a high melting point and good high-temperature performance, and it has not found much literature when studying its role in HEA. Tungsten (W) is a good metal structural element in the periodic table of all refractory elements (e.g., Mo, V, Nb). Therefore, it can be incorporated into HEA to obtain high strength and low cost, and it has good mechanical properties and high-temperature applications. In recent days, much research has been going on to design new alloy systems with improved properties suitable for different engineering applications. Also, an ongoing effort is focused on empirically correlating the HEAs' phase evolution and thermodynamic parameters and understanding the structure-property relation. Therefore, the present research focuses on designing alloys by introducing varying tungsten elements with the transition elements to synthesize HEA, which has higher mechanical properties and better oxidation resistance. The detailed objective and results obtained are summarized as follows.

- Development of W- containing HEAs namely AlCrFeMnNiWx (x=0, 0.05, 0.1, 0.5 mol) via powder metallurgy and arc melting route.
- To explore the possibilities of hydrogen storage capability in the case of proposed HEA.
- To understand the effect of Tungsten on microstructure evolution and mechanical properties of proposed HEAs.

- Study of the oxidation behavior of HEAs at the temperature of 200°C, 500°C, 700°C, 800°C, and 850 °C to propose their suitable service temperature.
- To develop the mathematical model (ANN) for the properties prediction of this class of HEAs.
- To study the influence of different heat treatments on the microstructure and mechanical properties of the AlCrFeMnNiWx (x=0, 0.05, 0.1, 0.5 mol) HEAs

1.8 Outline of the Thesis

- **Chapter 1:** The present research work is split into 9 chapters, including introducing the high entropy alloys and a literature review on high-temperature properties.
- Chapter 2: Materials and method
- **Chapter 3:** Alloy Preparation Via Vacuum Arc Melting route, phase characterization, and properties have been described.
- **Chapter 4:** AlCrFeMnNiWx (x=0, 0.05, 0.1 and 0.5 mol) HEAs were synthesized by mechanical alloying. The effect of tungsten content on the phase evolution of HEAs was investigated. Also, phase formation of the present HEAs has been correlated with calculated thermodynamic parameters.
- **Chapter 5:** Synthesis and characterization of HEA powder for hydrogen storage. The absorption and desorption studies are discussed in detail.
- **Chapter 6:** Discusses Effect of Heat Treatment of processed HEAs on microstructure and mechanical properties of AlCrFeMnNiWx high entropy alloys.
- **Chapter 7:** High and low temperature oxidation behaviors of spark plasma sintered AlCrFeMnNiWx (x=0, 0.05, 0.1 & 0.5 mol) HEAs at different temperature are discussed.
- **Chapter 8:** Application of ANN Approach to predict different properties are discussed.
- Chapter 9: Conclusions and suggestions for future work are given in the last chapter.

This chapter demonstrates an extensive overview of the research problems and objectives in order to achieve the goal. Based on the above discussion, the author executes the experimental studies and finding meaningful results. Before proceeding with the result and discussion, it will be necessary to describe the material and method that have been adopted in the experiment work and explain in the next chapter.

Chapter 2

MATERIALS AND METHODS

This chapter discusses about the materials and methods implemented for the preparation of AlCrFeMnNiWx (x= 0, 0.05, 0.1 and 0.5 mol) HEAs.

2.1 Materials Preparation

2.1.1 Preparation of AlCrFeMnNiWx (x= 0, 0.05, 0.1 and 0.5 mol) HEAs by Arc melting route

The multicomponent AlCrFeMnNiWx (x=0, 0.05, 0.1 and 0.5 mol) HEAs (henceforth designated as A1, A2, A3, and A4) were prepared by solidification technique with a mixture of high purity metals (> 99.7%) under high purity argon environment. The alloy was melted at least five times to obtain chemical homogeneity.

2.1.2 Preparation of AlCrFeMnNiWx (x= 0, 0.05, 0.1 and 0.5 mol) HEAs powders

High purity (> 99.5% of Alpha aser) metal powder was utilized for the blend of AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs. At first, the blend of metal powder has been processed by planetary ball process Pulverisette-P6 (Fritsch, Germany) within the damp condition where toluene was utilized as a process control agent (PCA) along with side the10 mm tungsten carbide balls. The BPR (ball to powder proportion) has been kept up with the proportion 10:1. A small amount of milled powder had collected after 10 minutes for reference, and an interval of each five-hour was maintained.

2.1.3 Spark plasma sintering of AlCrFeMnNiWx (x= 0, 0.05, 0.1 and 0.5 mol) alloys powders

The mechanically alloyed nanocrystalline HEAs powder prepared by 20 h s of milling time has been used for the SPS experiment to obtain a bulk pellet. The SPS is a rapid compaction technique for engineering materials, aiming to achieve the metallic bonding between the particle [69]. A high DC electric supply and uniaxial pressure have been used simultaneously for the sintering process. A pair of graphite die has been used between the punches and powder samples. Moreover, all the setup has been encapsulated in a vacuum chamber. It is recommended that less holding time and lower temperatures should be applied to get less grain growth and better properties [187]. Synthesis of material by Vacuum arc melting route

The multicomponent AlCrFeMnNiWx (x=0, 0.05, 0.1, and 0.5 mol) HEAs (henceforth designated as A1, A2, A3, and A4) were prepared by solidification technique with a mixture of high purity (~ 99.5) metals under a high purity argon environment. The alloy was melted at least five times to obtain the chemical homogeneity. Then a copper mold has been utilized for cooling purposes.

2.2 Characterization of HEAs

Different characterization techniques were used to analyze the phase evolution in AlCrFeMnNiWx alloys. The methods were discussed in subsequent paragraphs.

2.2.1 Density measurement of spark plasma sintered sample

Theoretical density has been calculated by the rule of mixture given by Eq. 2.1 [3]:

$$\rho_{th} = \rho_m \cdot (1 - V_f) + \rho_f \cdot V_f \dots \dots (2.1)$$

Where ρ_{m} and ρ_{f} are the densities of matrix and filler and V_{f} is the volume fraction, respectively.

The Archimedes principle determined the densities of sintered samples using a density measurement apparatus and precise weighing balance with the accuracy of ± 0.1 mg. Ethanol as a media was used to determine the alloys' bulk density. Eq calculated the density. 2.2 [3]:

$$\rho_{\exp} = \left[\begin{pmatrix} W_{air} / \\ W_{air} - W_{med} \end{pmatrix} \right] \rho_{med} \dots (2.2)$$

 $W_{_{air}}$ and $W_{_{med}}$ are the weight of the sample in air and medium, respectively, the $\rho_{_{med}}$ is the density of the medium.

2.2.2 Phase evolution studies using XRD

The X-ray Diffraction (XRD) was performed on mechanically alloyed metal powder to investigate phase characterization via BRUKER D2 PHASER (with Cu radiation target, λ =0.154056 nm) instrument operating at 45 kV and 30 mA having 2 Θ ranging from 20 to 90° and at a scan speed of 3°/min. XRD has been performed to study the phase evolution both after Mechanical Alloyed and sintering samples. Also, crystallite size, lattice parameter, and lattice strain are calculated through the Scherrer equation by using the XRD data. The instrumental broadening was corrected using a single crystal Si wafer.

$$D = \frac{k\lambda}{\beta\cos\theta}.....(2.3)$$

Where D is the crystallite size, K is the shape factor (~ 1), λ is the wavelength of X-Ray, β is the line broadening, θ is the Bragg angle.

2.2.3 Microstructure characterization by scanning electron microscopy (SEM)

The microstructural characterization was carried out by scanning electron microscopy, equipped with the energy dispersive spectroscopy (EDS) by JEOL JSM - 7610 and NOVA, NANOSEM 450. The SEM and backscattered modes have been employed with a voltage 5 kV and 20 kV. The powder sample after the milling process, the powders were prepared by dispersing using the ultrasonicator instrument and spread in sticky carbon tape that has been analyzed under SEM. The bulk pallet samples after the SPS were prepared by grinding using different abrasive paper (SiC – 120 to 1200 grit size) prepared by grinding on an abrasive wheel. For a better Mirror finish of the alloy surface, a velvet cloth has been used along with alumina slurry (particle size up to 0.25μ m) and dispersive oil. Additionally, the samples are cleaned and dried further. The point and area EDS data were obtained from at least 5 points, and each element's atomic percentage was carried out.

2.2.4 Thermal Behavior study by DSC and TGA

The HEAs that are prepared by spark plasma sintered samples are examined up to 900°C with a heating rate of 10°C/min. A PerkinElmer Differential Thermal Analysis (DTA, STA 6000) has been utilized to understand the HEAs' phase stability with respect to temperature in a nitrogen environment. The baseline was corrected before acquiring the temperature curve for each alloy. For all the alloy samples, the data were acquired repeatedly 2 times to check the reproducibility of the results.

A thermal gravimetric analyzer (TGA, Netszch Tursus TG209) has been utilized for examined the spark plasma sintered samples. To observe the high-temperature stability, temperature ranges are 30 to 900°C have been chosen in a nitrogen environment. During the experiment, the nitrogen flow has been kept in purge as 20ml/min. HEA powder sample has also been performed for the desorption of the hydrogen gas in a different study at different heating rates up to 400°C. The heating rate was 5 K/min, 10 K/min, and 15 K/min. Activation energy has also been calculated based on different heating rates of the TGA curve with the help of the Kissinger relation.

2.3 Hydrogenation study

2.3.1 Alloy Preparation

Powder sample is prepared using high-energy ball milling from pure materials (with 98% to 99.9% purity). The metallic elements (total 40 g) are kept in the milling vial (capacity of 250 cm³) with the 41 tungsten coated balls for maintaining 10:1 BPR (Ball to Powder Ratio) along with the Process Control Agent (PCA), i.e., toluene (C_7H_8) for preventing cold welding during the milling process. A Fritsch pulverisette 6 planetary ball mill was used to pulverize the sample with the speed of 300 rpm for 20 hours (with clockwise 30 min milling time, then 15 min dwells and again 30 min with anti-clock rotation).

2.3.2 Details of experimental setup and characterization of HEA powder

After successfully preparing high entropy alloy, the X-Ray Diffractometer has carried out the structural characterization (Bruker D2 PHASER, Cu-Ka) technique. A Scanning Electron Microscope (SEM, FESEM, Carl Zeiss Supra 55) is used to study surface morphology. A Thermogravimetric Analyser (TGA, Netzsch Tarsus 209) is used for the desorption of hydrogen from alloy. For the hydrogen absorption study, an experimental setup based on the gravimetric method is fabricated, as shown in Fig. 2.1. The setup consists of pipelines for gas flow fabricated using ¹/₄ inch tubes, medium pressure below sealed valves to control gas flow, a hydrogen container with a pressure indicator, a perfectly sealed reactor with a filter assembly with provision for a thermocouple. More details about the reactor are given in the author's previous article [90]. Before the start of the absorption experiment, the full setup is checked for leak-proof using argon gas. Also, the alloy is activated at 200°C and a vacuum pressure of 10⁻³ mbar before the absorption process. First of all, the weight of the reactor with alloy is measured using a weighing machine (Essae DS 852G, ± 0.01 g accuracy), and then the reactor is connected to the setup. After that, the hydrogen container is filled with hydrogen at a predefined pressure and then using control valves, hydrogen is allowed to flow to the reactor (alloy) maintained at a constant temperature. The absorption of hydrogen takes place in the reactor; meanwhile, the generate reaction heat is removed. Once the system reached equilibrium condition, the reactor is de-attached from the setup and measured the weight increase. The difference in weights gives the mass of hydrogen absorbed in the high entropy alloy.



Figure 2.1 Experimental setup for hydrogen absorption measurements

2.4 Heat treatment of proposed HEAs

The heat treatment of samples has been performed in the Nabertherm tubular (RSV 120-500/13) furnace in a vacuum environment at a temperature of 800°C, 1000°C, and 1200°C for 4 hours (a schematic diagram shown in Fig. 2.1). After the heat treatment, samples were left in the furnace environment for slow cooling purposes. Finally, samples are cut and ground through the different polishing papers (#200 to #2000) for metallographic analysis.



Figure 2.2 Heat treatment cycle

2.5 Mechanical Testing of proposed HEAs

2.5.1 Microhardness of proposed HEAs

Vickers hardness measurements were performed by UHL VMHT (Walteruhl GmBH, Germany) on bulk AlCrFeMnNiWx (x= 0, 0.05, 0.1, and 0.5 mol) HEAs. The load of 200 gf and dwell time

of 15 sec were applied to take the hardness of the bulk alloys. The hardness is given by Eq. 2.4 [80]:

Where F is the load applied, and d is the diagonal of the indentation.

The hardness test was performed at 8 different positions in the same alloy to check the reproducibility.

2.5.1 Room temperature nanoindentation study

A nanoindentation test was used to identify nanomechanical behavior on the alloy. All the nanomechanical study was carried out in Hysitron triboindenter TI 750, which is fitted with a three-sided pyramid Berkovich indenter with a tip radius of 150 nm. Open-loop and displacement control mode (loading-holding-unloading) using a single cycle indentation testing technique has been applied for the test purpose. Minimum 9 indent points have been selected to maintain a good correlation of the output data, and a distance of a minimum of 15µm has been kept from each other in $30 \times 30 \ \mu m$ array. The maximum load during the test is 5000 μN at a rate of 250 $\mu N/s$. Ten seconds of dwell time being chosen for the indentation creep study. The calibration has been performed before the test. It is ensured that there is no error occurred due to the indenter tip and machine operation. The average value has been taken for the plotting of the load-displacement curve for further study

2.6 Oxidation Study of proposed HEAs

The spark plasma sintered sample has been shaped by the wire EDM cutter for the oxidation study. The shaped sample has been polished for removing the dirt and oil which formed during the different simple preparation processing. TGA (Thermal Gravimetry Analyser, Netszch tarsus TG209) was used for oxidation analysis. The exposure time of samples was 50 hours, while different temperatures are 700°C, 800°C, and 850°C have been chosen for the study. During the experiment, N₂ gas has been used as a protective gas against the environment at a flow of 20 ml/min.

2.6.1 Phase, surface morphology, and Raman analysis of oxidized samples

The phase of different oxides after oxidation were characterized by XRD using an X'pert Pro (Panalytical, USA) X-ray diffractometer unit with a Cu-K α (λ =0.1540598 nm) source.

Instrumental broadening was corrected using a single crystal Si wafer. Then, the morphology of the high entropy alloy's oxide surface was studied using FE-SEM (JEOL JSM - 7610 SEM) operated at 30 kV Immediately after the oxidation. Furthermore, the oxide layer has been evaluated by Raman spectroscopy at a wavelength of 532 nm.

This chapter discussed the material and method used in the current research work. By using the above material and method, different experiments have been designed and performed. The comprehensive results and discussions of the current research work are explained in the following chapters.

Chapter 3

SYNTHESIS AND CHARACTERIZATION OF AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol)

HEAs PREPARED BY ARC MELTING ROUTE

This chapter presents the detailed structural and microstructural characterization of AlCrFeMnNiWx (x = 0, 0.05, 0.1, and 0.5 mol) HEAs with the combined thermodynamic simulation approach. Moreover, the effect of tungsten on the HEAs prepared by arc melting route is also investigated to understand the microstructure and mechanical properties of the proposed HEAs.

3.1 Thermodynamic parameters and simulation

It is important to note here that different thermodynamic parameters predict the formation of solid solution phases. A parameter, Ω , was earlier proposed [59] to get the mutual influence between ΔH_{mix} and ΔS_{mix} , which provides the guideline for the prediction of phase formation in designing multi-component alloy. The formation of the BCC or FCC solid solution phases also depends upon the valence electron concentration (VEC). The quantitative prediction of the formation of the BCC or FCC phases in HEAs was predicted by Guo et al. [61] using VEC parameters. All the physiochemical and thermal properties for the investigated HEAs are calculated [188] and presented in Table 3.1.

The thermodynamic simulations of AlCrFeMnNiWx (x = 0, 0.05, 0.1 and 0.5) have been carried out by ThermoCalc® software using the TCHEA2 database to predict the phase formation. Phase fraction Vs. temperature plot of AlCrFeMnNiW_x (x = 0, 0.05, 0.1 and 0.5) is shown in Fig.3.1. It is to be noted that in the case of AlCrFeMnNi HEA, BCC_B2 (β 1) and BCC_B2#2 (β 2) are found to form from the liquid phase, and SIGMA-phase (σ) is formed during solid-state transformation. Similarly, AlCrFeMnNiWx (x = 0.5) HEA indicates that BCC_B2 (β 1) and BCC_B2#2 (β 2) phases are also formed from the liquid phase, and the remaining phases such as SIGMA-phase (σ), MU_PHASE, MU_PHASE#2 are evolved during solid-state transformation.


Figure 3.1 Thermodynamic simulation of AlCrFeMnNiWx (X=0, 0.05, 0.1 and 0.5 mol) HEAs A1, A2, A3 and A4 respectively.

It is found that the Ω values increase with the addition of W. The constant increment of the Ω ; concerning W content in the studied HEAs is a signpost for the active solid solution formation. Similarly, δ value also decreases with W addition, leading to increased lattice distortion energy.

| | Dhaga | Dhaga | ΔH_{mix} | ΔS_{mix} | T _m | Ω | δ | VEC | Λ |
|-----------------------------|-----------|----------|------------------|----------------------------------|----------------|------|------|------|---------|
| Alloys | Pliase | Phase | (KJ/m | (JK ⁻ | (°C) | | (%) | | (J/mol/ |
| | predicted | existing | ol) | ¹ mol ⁻¹) | | | | | K) |
| AlCrFeMnNi | BCC_B2, | BCC, B2 | -6.56 | 1.61R | 1361.2 | 3.33 | 5.38 | 5.20 | 0.461 |
| | BCC_B2#2, | | | | | | | | |
| | sigma | | | | | | | | |
| AlCrFeMnNiW _{0.05} | BCC_B2, | BCC, B2 | -3.921 | 1.64R | 1380.4 | 5.62 | 5.39 | 5.16 | 0.459 |
| | BCC_B2#2, | | | | | | | | |
| | Mu phase | | | | | | | | |
| | sigma | | | | | | | | |
| AlCrFeMnNiW _{0.1} | BCC_B2, | BCC, B2 | -2.994 | 1.67R | 1399 | 7.75 | 5.39 | 5.13 | 0.459 |
| | BCC_B2#2, | | | | | | | | |
| | Mu phase | | | | | | | | |
| | sigma | | | | | | | | |
| AlCrFeMnNiW _{0.5} | BCC_B2, | BCC, B2 | -2.816 | 1.76R | 1540 | 9.42 | 5.39 | 4.91 | 0.459 |
| | BCC_B2#2, | | | | | | | | |
| | Mu phase, | | | | | | | | |
| | sigma, Mu | | | | | | | | |
| | phase#2 | | | | | | | | |

Table 3.1 Predicted phase, existing phase, physiochemical and thermal properties of AlCrFeMnNiWx (X=0, 0.05, 0.1 and 0.5 mol) HEAs.

3.2 Structural characterization

Fig. 3.2 (A) shows the XRD pattern of the as-cast AlCrFeMnNiW HEAs in which all peaks are identified. A1, A2, A3, and A4. HEAs consist of BCC and ordered B2 phases [189]. Only two peaks were found with 2θ between the 20 to 100° in which a major peak with (110) plane and a minor peak (210) plane at without the addition of the W. The progressively increment of W content caused the obsoleting of peaks and form the single intense peak of BCC with (110) plane. The formation of a BCC structure is favored when most of the binary pairs present in the alloy crystalline in BCC lattice [97]. The position of the (110) plane is slightly shifted leftward with respect to the addition of W due to a change in the lattice parameter of the crystal. The progressive increment has been seen in the lattice parameter, which is mainly due to the larger atomic radius of the W in the HEAs. It is interesting to know that the lattice strain and crystallite size inversely progress to each other in Fig. 3.2(B). Initially, the lattice strain is increasing (up to X < 0.1). Reasoned factors are size mismatch factor between the constituent elements, increased grain boundary fractions, and mechanical deformations [190]. Subsequently, the reduction and

increments have been seen (X > 0.1) of lattice strain, and crystallite size, respectively, which is due to the dissolution of the W content reached the maximum solution limit in the BCC phase [191]. The average crystallite size, calculated by the Scherrer equation, is found to be 14nm.

Thus, making the BCC structure more favorable as it has a lower packing efficiency and can accommodate elements with a higher atomic volume without much distortion [23]. A large lattice distortion can be found due to the dissolution of the Al in the alloy, which tends to unsterilized the formation of BCC as well as the formation of the binary compound. Al has a higher negative enthalpy of mixing with the Cr, Fe, Mn, Ni, and W, i.e., -10, -11, -19, -22, and -2 kJ mol^{-1,} respectively [2]. It may be possible for the formation of a stable binary compound with AlNi and AlFe [192].



Figure 3.2 (A) XRD pattern of the as-cast AlCrFeMnNiW_x (x=0, 0.05, 0.1 and 0.5 mol) Alloys(B) The relationship between lattice parameter, crystallite size, and strain

3.3 Microstructure Characterization

The typical SEM results of the as-cast AlCrFeMnNiWx HEAs are shown in Fig 3.3 (A1 to A4). The EDS analysis (as given in Table 3.2) identifies the constituent phases in the microstructure. The surface morphology of AlCrFeMnNiWx HEAs consists of Fe-Cr-Mn rich (β 1) primary phase and Ni-Al-rich phase (β 2) secondary interdendritic phase. The interdendritic phase is observed to be weave-like morphology. Ma et al. [193] recently reported that weave-like morphology is common in BCC and B2 phases. Besides, Al affects the lattice constants strongly and leads to a large lattice misfit [193]. The Typical SEM images of the alloys (Fig. 3.3 A1, A2, A3, and A4) demonstrates mainly two dendritic phases with white contrast and grey contrast. It is also found that both dendritic phases undergo spinodal decomposition during solid-state cooling up to room temperature. The EDS data (Table 3.2) shows the composition information of different phases.

The dendritic phase is the Fe-Cr-rich dendritic phase, while the interdendritic region is the Ni-Al rich phase. It is evident from the microstructure that both the dendritic and interdendritic regions undergo spinodal decomposition during the solid-state cooling to up to room temperature. The bright contrast phase, i.e. one of the phases formed during the spinodal decomposition of primary Fe-Cr-Mn rich (β 1) is found to be Ni-Al rich phase, leading to the formation σ phase. This σ phase is not detected in the XRD pattern due to its low volume fraction. However, thermodynamic simulated results also indicate the formation σ phase during solid state transformation. Based upon structural and microstructural characterization, the sequence of phase formation in the investigated of the AlCrFeMnNiW_x (X= 0, 0.05, 0.1, 0.5 mol) HEAs are described as follows;

- (i) Primary dendritic phase: $L \rightarrow L + BCC$ Fe-Cr-Mn rich phase (β 1),
- (ii) Secondary dendritic phase: $L \rightarrow L + BCC$ Ni-Al-rich phase ($\beta 2$)
- (iii) Solid state transformation:
 - (a) BCC ($\boldsymbol{\beta}$ 1) \rightarrow BCC_B2 (α 1) + σ and
 - (b) BCC (β 2) \rightarrow BCC_B2 (α 2) + BCC (γ)



Figure 3.3 Typical SEM image of the AlCrFeMnNiWx (X=0 (A1), 0.05 (A2), 0.1 (A3), and 0.5

(A4)) HEAs

| | Regions | Al | Cr | Fe | Mn | Ni | W |
|-----------------------------|------------------------|-----------------|-----------------|-----------------|-----------|-----------|----------------|
| AlCrFeMnNi | D (White)(β1) | 21.30±0.1 | 14.73±0.2 | 19.90±0.2 | 22.10±0.5 | 21.97±0.1 | - |
| | ID (Grey)($\beta 2$) | 15.78±0.2 | 18.92±0.7 | 22.97±0.1 | 17.75±0.1 | 24.59±0.3 | - |
| AlCrFeMnNiW _{0.05} | D (White)(β 1) | 18.38±0.2 | 21.19±0.2 | 26.88±0.1 | 10.85±0.6 | 22.23±0.1 | 0.47 ± 0.1 |
| | ID (Grey) (β 2) | 18.64 ± 0.2 | 21.01±0.3 | 26.44 ± 0.4 | 11.37±0.1 | 22.00±0.2 | 0.5 ± 0.1 |
| AlCrFeMnNiW _{0.1} | D (White)(β 1) | 12.16±0.4 | 30.56±0.9 | 25.15±0.5 | 16.63±0.8 | 14.23±0.6 | 1.27±0.1 |
| | ID (Grey) (β 2) | 19.85±0.1 | $16.84{\pm}1.8$ | 17.88 ± 1.1 | 16.53±1.0 | 28.23±3.9 | 0.66 ± 0.1 |
| AlCrFeMnNiW _{0.5} | D (White)(β 1) | 11.8±0.7 | 20.9±1.1 | 25.40±0.3 | 26.07±0.8 | 14.31±0.5 | 1.53±0.4 |
| | ID (Grey)($\beta 2$) | 16.85±0.1 | 13.98±1.5 | 19.7±4.4 | 24.77±2.4 | 24.07±0.9 | 0.63±0.2 |

Table 3.2 Chemical composition of the elements (in at%) of as cast AlCrFeMnNiW_X (X = 0, 0.05, 0.1, 0.5 mol) alloys (D stands for the dendrite and ID for the interdendritic region).

The TEM study is required to confirm further the chemical composition of the $\alpha 1$, $\alpha 2$, γ , and σ phases.

3.4 Hardness Measurement and its divination using the ANN approach

Fig. 3.4 shows the Vickers hardness of the as-cast AlCrFeMnNiWx HEAs. The Vickers hardness of the studied HEAs without containing W (HEA A1) was found 552.7±22 and 461.26±38 in the interdendritic and dendritic regions, respectively. Noticeably, the addition of a small amount of the W in the alloy led to a reduction of the hardness in the alloy. Further addition of the W content improves the hardness of the alloy. Noticeably, the HEAs do not follow any sequence against the addition of the W contents. As per the EDS result, most of the W contents are occupied by the dendritic region while the phase fraction (A1>A2>A3>A4) in the region continuously decreases (see in Fig. 3.4). It might be a reason for various hardness values in the different regions of the A1, A2, A3, and A4 HEAs. The presence of BCC solid solution phases in the microstructure is attributed to the high strength of the materials. The empirical relation between the yield strength and hardness is given in equation (3.1) [24].

$$\sigma_{ys} = \frac{HV}{3} (HVN) \dots (3.1)$$



Figure 3.4 The value of Vickers hardness of the HEAs as a function of variation of W with the volume fraction given in the bar

Therefore, the studied HEAs with a composite microstructure consisting of harder BCC dendritic phase and lamellae morphology inside each of BCC phases could be considered as a potential candidate for high-temperature structural applications [172].

3.4.1 Dataset, training, and validation of ANN model

The collection of the 16 different alloy datasets was established based on previous work and present work, which followed a similar processing route, i.e., arc melting process. The alloys include Al, Cr, Mn, Fe, Ni, and W with the different compositions (wt.%) shown in Table 3.3. The aim of employing the ANN tool in this work is based on the magnitude of the hardness increment, and decrement mainly depends upon the alloying element and composition [194][195].

| Alloying elements | Al | Cr | Fe | Mn | Ni | W | Hardness (HV) | Ref |
|----------------------|-------|-------|-------|-------|-------|---|------------------|-------|
| 1 | 5.4 | 17.83 | 38.29 | 21.97 | 16.77 | 0 | 420 | [196] |
| 2 | 7.78 | 19.99 | 21.47 | 0 | 50.77 | 0 | 315.7 | [197] |
| 3 | 13.17 | 21.15 | 22.71 | 0 | 42.97 | 0 | 543.9 | [197] |
| 4 | 21.41 | 22.92 | 24.62 | 0 | 31.05 | 0 | 638.6 | [197] |
| 5 | 27.22 | 24.28 | 26.08 | 0 | 21.93 | 0 | 738.4 | [197] |

Table 3.3 The hardness of different alloys with the alloying composition (wt.%)

| 6 | 35.77 | 26.01 | 27.94 | 0 | 10.28 | 0 | 842.7 | [197] |
|----|----------------|-------|-------|-------|-------|------|--------|-------|
| 7 | 10.61 | 20.45 | 6.59 | 0 | 62.34 | 0 | 415.7 | [197] |
| 8 | 10.68 | 20.58 | 18.79 | 0 | 49.95 | 0 | 559.9 | [197] |
| 9 | 10.47 | 20.7 | 30.01 | 0 | 38.55 | 0 | 559.6 | [197] |
| 10 | 10.8 | 20.8 | 40.22 | 0 | 28.18 | 0 | 510.2 | [197] |
| 11 | 10.84 | 20.9 | 49.38 | 0 | 18.87 | 0 | 537.2 | [197] |
| 12 | 10.9 | 21.01 | 59.79 | 0 | 8.3 | 0 | 580.3 | [197] |
| 13 | 10.86 | 20.93 | 22.48 | 22.11 | 23.62 | 0 | 552.7 | * |
| 14 | 10.47 | 20.18 | 20.67 | 21.32 | 22.78 | 3.59 | 502.92 | * |
| 15 | 10.11 | 19.49 | 20.93 | 20.59 | 22 | 6.89 | 490.15 | * |
| 16 | 7.95 | 15.32 | 16.45 | 16.19 | 17.29 | 26.8 | 461.26 | * |
| | * present work | | | | | | | |

One of the significant advantages of the ANN can be learned from the sample dataset. Thus, the training of the model is done by the ANN in which the network is adjusted to minimize the error to obtain high accuracy. Here, the training has been made at 60%, testing at 20%, and validation at 20% of the dataset. Several trails have been made with different numbers of neurons in the hidden layer, which is progressively increased from the small numbers of the neurons. The number of neurons has been selected based on the least mean square error (MSE) for the training, validation, and testing [198]. After many trials, the model has been fully trained for the prediction of the hardness. The finalized model has a 6-6-1 neuron system (6 neurons in the input layer, 6 in the hidden layer, and 1 in the output layer). But before applying, the prediction needs to be validated and tested with the experimental data. Due to the variation of values between alloying elements, feature scaling is also performed before feeding into the input layer of ANN. The generalized formula for performing feature scaling is given in equation (3.2).

$$x_{scale} = \frac{x_i - mean(x_i)}{std(x_i)}....(3.2)$$

Where x_i is a column vector which contains the values of ith element in the alloy and $i \in 1, 2, 3, \dots, n$.



Figure 3.5 (A) MSE convergence during the training of the ANN model for the hardness prediction (B) Comparison of the hardness value with experimental and predicted by the ANN

model

At the end of the training, Mean Square Error (MSE) is also calculated between the target values and desired output values[199]. The ANN model is successfully developed with a backpropagation convergence technique by Levenberg- Marquardt training algorithm. The neural network training performance curve is shown in fig 3.5(A), where the convergence to mean error of 8.51×10^{-3} is saturated at the second epoch. Fig 3.5(B) represents the comparison between the experimental hardness value with the ANN predicted value.

3.4.2 ANN analysis

The impact of the alloying element on the alloy hardness could understand, a dataset used for training and validation followed by the testing of the model (as shown in Fig 3.6). In Table 3.4, the presentation of the ANN predicted hardness and experimental hardness had been given. It is seen that the ANN for hardness can not only perform training (R= 0.887) but also validate (R= 0.999) with the best test sets (R=0.946). The ANN gives satisfactory results in comparison with the experimental data. An error of the predicted value of 6.46 % with the accuracy of the prediction of 93.54% is obtained. The overall ANN model simulation result is calculated R=0.941, which is an excellent correlation for predicting the hardness at the available dataset.

Table 3.4 The experimental and predicted value of hardness by the ANN model

| Experimental | ANN | % error | % Accuracy |
|--------------|----------|----------|------------|
| 420 | 392.9036 | 6.451518 | 93.548482 |

| 315.7 | 346.7834 | 9.845867 | 90.154133 |
|--------|----------|----------|-----------|
| 543.9 | 496.6284 | 8.691229 | 91.308771 |
| 638.6 | 654.1533 | 2.435535 | 97.564465 |
| 738.4 | 749.5287 | 1.507139 | 98.492861 |
| 842.7 | 835.0943 | 0.902534 | 99.097466 |
| 415.7 | 383.2123 | 7.81517 | 92.18483 |
| 559.9 | 420.9459 | 24.81766 | 75.182344 |
| 559.6 | 457.1692 | 18.30428 | 81.695718 |
| 510.2 | 499.4807 | 2.101008 | 97.898992 |
| 537.2 | 539.296 | 0.390162 | 99.609838 |
| 580.3 | 590.2696 | 1.71801 | 98.28199 |
| 552.7 | 516.1824 | 6.607125 | 93.392875 |
| 502.92 | 490.34 | 2.501387 | 97.498613 |
| 490.15 | 457.6617 | 6.628246 | 93.371754 |
| 461.26 | 473.4339 | 2.63927 | 97.36073 |
| Averaş | ge | 6.459759 | 93.540241 |



Figure 3.6 Presentations of the hardness prediction by ANN model against the experimental hardness results

A similar study of property-oriented material design strategy combining machine learning, experiment design, and feedback from the experiment to achieve the high hardness HEA has also been seen [200]. An advanced study will generate more hardness in the case of HEAs to train and predict the hardness and other mechanical properties using the ANN-based approach.

3.4.3 Sensitive analysis

Sensitivity analysis has been used to understand the effect of input parameters, i.e., alloying elements, on the output parameter, i.e., hardness values of the considered HEAs. A fully developed ANN model has been used in this sensitivity study where only one parameter has been varied at a time while keeping other parameters constant [201]. The sets of input parameters with minimum values are considered the minimum value set, and that having maximum values is called the maximum value set [202].



Figure 3.7 Sensitivity analysis for the different alloying composition of (A) Al, (B) Cr, (C) Fe, (D) Mn, (E) Ni, and (F) W by the ANN hardness prediction model

In the sensitivity analysis of the Al, the input parameter of the Al is varied, and other parameters are kept constant for the minimum value set and maximum value set. However, the amount of the total composition (wt%) of the alloy increased and decreased accordingly during the sensitivity analysis. Here, the sensitivity analysis aims to understand the behavior of the model by fluctuating the individual elemental composition. Furthermore, the dataset fed in the model for the output values as a form of hardness (HV). Similar methods are used for each alloying element and represent in Fig. 3.7.

The impact of Al on the hardness of the HEAs can understand that the trend of the minimum and maximum set value lines is almost similar (Fig 3.7A). Therefore, the change in the input parameter will lead to a significant output by the ANN developed model. Similarly, the Fe and Ni (Fig. 3.7C and Fig. 3.7E) also provide more significant output. In Fig. 3.7B, D and F have less significance as compared to others. The less significant output value is mainly due to prediction errors, which are because of a smaller number of datasets during the training, validation, and testing.

3.5 Summary

- The multicomponent AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs are developed through melting and solidification route and thermodynamic simulation was utilized for phase prediction.
- SEM and XRD results reveal the formation of the BCC Fe-Cr-Mn rich (β₁) primary phase and BCC Ni-Al-rich phase (β₂) interdendritic dendritic phase. BCC (β₁) dendritic phase undergoes spinodal decomposition to form a mixture of BCC_B2 (α₁) and σ phases. While BCC (β₂) interdendritic phase also undergoes solid-state transformation to form BCC_B2 (α₂) and BCC (γ) phases.
- The estimated maximum hardness of 552.7 ± 22 HV is strongly dependent on W as a minor alloying element in the investigated HEAs.
- The ANN gives satisfactory results in comparison with the experimental data. An error of the predicted value of 6.46% with the accuracy of the prediction 93.54% is obtained.

The powder metallurgy route has also been adopted to synthesize AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs to understand the effect of the processing route on the microstructure evolution and hardness of the proposed HEAs. Next chapter will focus on synthesis and characterization of proposed HEAs prepared via mechanical alloying followed by spar plasma sintering (SPS).

Chapter 4

SYNTHESIS AND CHARACTERIZATION OF AlCrFeMnNiWx HEAs BY POWDER METALLURGY ROUTE

The present chapter explores the synthesis of nanocrystalline tungsten-containing AlCrFeMnNiW_x (x= 0, 0.05, 0.1, 0.5 mol) high entropy alloys (HEAs) by mechanical alloying with subsequent spark plasma sintering (SPS). The microstructure, thermal stability, and mechanical properties of designed HEAs are critically analyzed and discussed in detail in this section.

4.1 Thermodynamic parameters for solid solution formation

It is important to note that the phase formation in HEAs is explained by using various thermodynamic parameters. One such thermodynamic parameter is Ω , which defines the mutual influence between ΔH_{mix} and ΔS_{mix} It provides the guideline for the prediction of phase formation when designing a multi-component alloy [59], and it is described in chapter 1.3 [60]. A geometric parameter (Λ) is also significant for understanding the complexity and formation of disordered solid solution (DSS) in multi-component alloys, which can be calculated by equation (4.1) [203].

Based on the above mention equations, All the physiochemical and thermal properties are calculated and given in Table 4.1. However, these rules are mainly favored to alloys that have a similar crystal structure, atomic size, valency electron, and electronegativity [204].



Figure 4.1 (a) shows the plot of Ω and δ as a function of the variation of tungsten content, and(b) indicates the plot of VEC w.r.t. tungsten content of studied HEAs.

The thermodynamic parameter, Ω values, increases with the addition of W-content (as shown in Fig. 4.1a), which is a signpost for the active solid solution formation. Similarly, the size difference parameter δ value also increases with the W addition, which increases the lattice distortion energy of the solid solution. From Table 3.1, it is concluded that the addition of the tungsten element leads to the formation of a stable BCC solid solution phase in studied W-containing AlCrFeMnNiWx (x= 0, 0.05, 0.1, 0.5 mol) HEAs due to decreasing in the VEC parameter from 6.80 to 6.20. Zhang [205] proposed the criteria for the formation of a solid solution phase by the thermodynamic Ω parameter and atomic size factor δ parameter (i.e., $\Omega \ge 1.1$ and $\delta \le 6.6\%$). Since both parameters are satisfied to form solid solution phase in AlCrFeMnNiWx (x= 0, 0.05, 0.1, 0.5 mol) HEAs. A geometric parameter (Λ) is also calculated to describe the range of the disorder solid solution (DSS) phase formation, which indicates the formation of single-phase DSS ($\Lambda > 0.96$), two-phase mixture (2.4 < $\Lambda < 0.96$), and mixture with compound ($\Lambda < 0.24$) [203].

4.2 Phase evaluation and morphology of ball-milled AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs powder

The phase formation, morphology, and size of HEAs powder at the initial stage (i.e., 10 minutes milling time) as well as at different milling times have been investigated using XRD and SEM. Fig. 4.2 shows the XRD patterns of investigated AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs at a different stage of the mechanical alloying process. Initially, the alloying process can be seen in the first 10 minutes, which is taken as the reference for the various alloying elements in the

studied HEAs. The diffraction peaks of the HEAs can be identified easily with the pattern of pure elements. The decrease in XRD peak intensity and increase in its width has also been observed in the first 5 hours of milling. At the same time, all the peaks correspond to the Al element disappear and form a less intense peak of Ni, Fe, Cr, and this trend was observed at all HEAs except Fig. 4.2d. The studied HEAs with x=0.5 show a small peak of the FCC solid solution phase at the first 10 h of milling, but it dissolved completely later. Hence, it is essential to note that by introducing more tungsten contents in the HEA, the crystal structure of the final pulverized powder reshuffle itself into the BCC. The dissolution of the XRD peaks corresponding to each element and merge with a single peak confirms a solid solution phase. The reason behind the dissolution is attributed to the mechanical alloying process, i.e., mainly cold welding, fracture, and rewelding of powder particles.



Figure 4.2 XRD patterns of the ball-milled AlCrFeMnNiW_x {x=(a) 0, (b) 0.05, (c) 0.1 and (d) 0.5} Alloys powders

As the milling hour increases, a less intense and broad peak has been observed in alloys, while alloy containing a high amount of tungsten (in Fig. 4.2d), a small peak corresponding to the FCC solid solution phase is observed. Further increase of milling, the formation of the FCC solid solution phase is suppressed, and several peaks corresponding to BCC solid solution phase have been obtained after the 15 hours of the milling process. However, the broad peak of the BCC solid solution phase and a minor peak of the FCC phase is seen in the remaining alloys after 20 hours of mechanical milling. Noticeably, the lattice strain increases w.r.t milling time, which is mainly



Figure 4.3 Typical SEM micrographs of AlCrFeMnNiW_x {x=(a-e) 0, (f-j) 0.05, (k-o) 0.1 and (p-t) 0.5} ball-milled high entropy alloy powder at different milling hour (10 minutes, 5 h, 10 h, 15 h and 20 h)

due to an increase in dislocation density produced by severe plastic deformation during the mechanical alloying process [206].

The SEM micrographs of W-containing AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs after 10min, 5 h, 10 h, 15 h and 20 h of milling are given in Fig. 4.3 (a-t), respectively. It is observed that the particle size reduces with milling time. Initially, the morphology of HEAs powder is faceted and irregular in size ranging from 30 to 50 µm. It is to be noted that at the initial stage of milling, the powder particle gets flattened because of the high compressive force exerted by the collision of W-balls. Subsequently, after 5 h of milling, a change of the shapes of individual powder particles has been observed due to the micro forging as well as the bunch of the powder particles being obstructed repeatedly between the milling balls with high kinetic energy.



Figure 4.4 Typical plots of (a) Crystallite size and (b) Lattice strain as a function of milling time

Furthermore, at the intermediate stage of the milling process, such as after the 10 h and 15 h milling time, the cold welding takes place [60]. The powder constituents reduce the diffusion distance into the micrometer range. The repeated cold welding and fracturing of the powder particle always increases the contact area along with the new surfaces of the powder particle, which ignites the reaction kinetics [75]. At the final stage of the milling process, i.e., at 20 h of milling time, a relative refinement and homogeneous microstructure of particle size have been observed on the microscopic scale. Fig. 4.4 shows the plot of crystallite size, strain w.r.t. milling time, which is also a piece of primary evidence for the pulverization of HEAs powder. The continuous decrease in crystallite size and increasing lattice strain due to distortion is observed during the milling

process progression. Thus, the average crystallite size of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs is found to be approx.10 – 15nm after the 20 h of milling, which is calculated by Scherrer equation ($D = \frac{0.9\lambda}{\beta \cos \theta}$, where λ is X-ray wavelength, and β is line broadening at FWHM).

4.3 Densification of ball-milled AlCrFeMnNiWx (x=0, 0.05, 0.1, 0.5 mol) HEAs powders

The mechanically alloyed nanocrystalline HEAs powder prepared by 20 h s of milling time has been used for the SPS experiment to obtain spark plasma sintered pellet. The SPS is a rapid compaction technique for engineering materials, which aims to achieve the metallic bonding between the particle [69]. A high DC electric supply and uniaxial pressure have been used simultaneously for the sintering process. A pair of graphite die has been used between the punches and powder samples. Moreover, all the setup has been encapsulated in a vacuum chamber. It is recommended that less holding time and lower temperatures should be applied to get less grain growth and better properties [187]. A schematic view has been represented in Fig. 4.5a, while Fig. 4.5b illustrates the holding time and the temperature during the sintering process of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs.



Figure 4.5 Schematic representation of (a) spark plasma sintering instrument, (b) Holding time for sintering process

In Fig. 4.6, systematic illustrations have also been presented to understand the densification behavior of the spark plasma sintered HEAs. It is worthy of mentioning that in solid-state sintering, the heating temperature should be $0.7T_{m}$, where the T_{m} is the melting point of the alloy powder

[17]. Initially, the formation of point contact between the particles and metallic bonding has occurred. In further stages, the formation of the neck, as well as grain growth, occurs. The reduction of pore size between the particles has also been observed. For better understanding, the formation of different phases, as designated clearly in Fig. 4.6c and d.



Figure 4.6 Schematic representation of (a) As a milled powder, (b) point contact during the initial stage of sintering, (c) Neck formation, and (d) Neck growth with the sintering temperature

4.4 Phase evaluation and morphology of spark plasma sinteredAlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs

Fig. 4.7 represents the XRD patterns of the spark plasma sintered HEAs at 900°C. It is found that the XRD pattern of AlCrFeMnNiW₀ HEA shows mainly the presence of three phases, such as BCC solid solution phase (β), FCC phase (α), and chromium-rich sigma phase (σ). Several minor peaks of the σ - phase have been observed in the spark plasma sintered AlCrFeMnNiW_x (x=0) HEA. The formation of BCC B2 phase, which is AlFe type ordered BCC (JCPDS: 00-033-0020 with a lattice parameter of 290.37 pm) is observed, while the σ -phase has a tetragonal structure (JCPDS: 01-071-7530 with a lattice parameter of a = 879.66 pm and c = 455.82 pm) [207]. It has been observed that the XRD peak intensity increasing progressively by alloying of W-content, which indicates more ordered arrangements in the AlCrFeMnNiW_x (x = 0, 0.05, 0.1, 0.5 mol) HEAs. The lattice parameters of different phases have been given in Table 4.2. The fraction of the FCC phase has been evaluated as 42%. 18%, 17% and 20% for the AlCrFeMnNiW_{x=0}, AlCrFeMnNiW_{x=0.05}, AlCrFeMnNiW_{x=0.1}, and AlCrFeMnNiW_{x=0.5} respectively. On the other hand, the reduction of volume fraction of the FCC solid solution phase (α) has been detected in the AlCrFeMnNiW_x (x=0.05, 0.1, 0.5 mol) HEAs. It is worthy to note that the phase formation rule is significantly worked given by Guo et al. [208]. In addition, the formation of the σ -phase (intermetallic compound) also fulfills the criteria of the geometry parameter (0.24 < Λ < 0.96), as proposed by Anil et al. [203].

It is also found that the FCC solid solution phase (standard pattern JCPDS# 00-001-1258) is mainly due to Mn, Ni, Cr-rich content because Ni and Mn are FCC stabilizers, which is similar to



Figure 4.7 XRD patterns of the spark plasma sintered AlCrFeMnNiW_x (x=0,0.05,0.1 and 0.5 mol) HEAs

Al_xCrFe_{1.5}MnNi_{0.5} HEA as reported by Saurav et al. [78, 209]. Simultaneously, the formation of σ -phase and detection of ordered B2 phase has been seen in the XRD pattern with the addition of W content. It is to be noted that the W atom produces the massive lattice distortion in the FCC solid solution phase due to its large atomic radius of Fe, Cr, and Ni. Hence, it minimizes the lattice strain energy and the presence of the W element in the HEAs. It promotes the formation of the BCC solid solution (standard pattern JCPDS# 96-152-5356) phase [210, 211], which corroborates with the phase formation prediction by the VEC thermodynamic parameter in the current studied W-containing HEAs. Further, it is observed that the increment of the W contents in studied HEAs completely stabilized in the BCC B2 solid solution phase.

| | | Phase | Phase existing | Lattice constant (pm) | | |
|-----------------------------|------------------|------------------------|----------------------|-------------------------------|-----|--|
| Sample | Predicted Phase | existing (after MA) | (after sintering) | $a = d\sqrt{h^2 + k^2 + l^2}$ | | |
| | | (41001 1111) | 5g) | BCC | FCC | |
| | BCC_B2, | | BCC, B2, | | | |
| AlCrFeMnNi | BCC_B2#2,Mu | BCC, FCC | FCC, σ- | 285 | 358 | |
| | phase, sigma | | sigma | | | |
| | BCC_B2, | | BCC, B2, | | | |
| AlCrFeMnNiW _{0.05} | BCC_B2#2, sigma | BCC, FCC | FCC, σ- | 288 | 370 | |
| | | | sigma | | | |
| | BCC_B2, | BCC, FCC | BCC, B2, | | | |
| AlCrFeMnNiW _{0.1} | BCC_B2#2, | | FCC, σ- | 295 | 370 | |
| | Mu phase, sigma | | sigma | | | |
| | BCC_B2, | | BCC B1 | | | |
| AlCrFeMnNiW0.5 | BCC_B2#2, | RCC ECC | ECC, B_{2} , | 295 | 369 | |
| | Mu phase, sigma, | BCC, FCC | ree, o- | 2)5 | 507 | |
| | Mu phase#2 | | sigina | | | |

Table 4.1 The phase prediction, existing phase, Lattice parameters of spark plasma sintered AlCrFeMnNi W_x (X=0, 0,05, 0.1 and 0.5 mol) HEAs

AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs at 900°C. In the backscattered electron (BSE) image, it is found the presence of two different phases with a distinct contrast in the sintered sample. One of the phases is AlFe type ordered (grey contrast marked as region '2') phase, and the other is the Cr-rich phase (brighter contrast marked as region '1'). While the small contents of the σ -phase have also been observed after the sintering, it is to be noted that the presence of Cr in spark plasma sintered HEA influences the formation of chromium-rich carbide and oxide phases [212]. The formation of the oxides or carbide in mechanical alloying is seen very often [213]. The EDS mapping reveals a small amount of carbon and oxygen has been observed in all HEAs, as shown in Fig. 4.9. However, there is no evidence of carbide/oxide was detected in XRD analysis in the HEAs.



Figure 4.8 Typical SEM micrographs of the spark plasma sintered AlCrFeMnNiW_x (x=0,0.05,0.1 and 0.5 mol) HEAs at 900°C



Figure 4.9 EDS mapping of the spark plasma sintered AlCrFeMnNiW_x (x=0,0.05,0.1 and 0.5

mol)

4.5 Thermal stability of spark plasma sinteredAlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs

The thermal stability of spark plasma sintered nanocrystalline HEAs is carried out using differential scanning calorimetry (DSC) at 900°C. Fig. 4.10(a) shows the curve between enthalpy and temperature, indicating no detection of the phase transformation in the studied spark plasma sintered HEAs up to 900°C. It is found that similar behavior has been observed in all studied AlCuCrFeMnNiW HEAs, which contain the same number of phases, such as BCC, FCC, and σ phase is no evidence of phase transformation up to 900°C. It is reported the combined effect of melting and decomposition of the AlFe (T_{melt}=1080°C) and decomposition of σ -phase at 930°C in the temperature range, 900 - 950°C [23]. In the AlCrFeMnNiW_x (x= 0.05) HEAs, a small endothermic (503°C) and exothermic peak (643.3°C) have been observed. It is found from the rule of mixture that the melting point of HEA is 1380.4°C (as mentioned in Table 3.1). However, the more number of mixing of elements led to more exothermic energy on the DSC experiment in a temperature range, which is due to the increment of lattice energy and grain boundary [190]. Further study needs to be performed to understand the high-temperature stability and precipitates dissolution of the AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs.



Figure 4.8 (a) DSC and (b) TGA curves of spark plasma sintered AlCrFeMnNiW_x (x=0,0.05,0.1, 0.5 mol) HEAs at 900°C

A dynamic thermal measurement has been performed to understand the oxidation behavior of the spark plasma sintered sample at a temperature from 30°C to 900°C via a thermal gravimetric analyzer (TGA). A curve has been plotted between TG (%) and temperature (°C) in Fig. 4.10(b). It is to be noted that during the experiment, N₂ gas is utilized as a protective gas at the flow of 20

ml/min. It has been observed that continuous mass gain indicates the surface oxidation of the sintered sample after 450°C. The spark plasma sintered AlCrFeMnNiW_x (x=0, 0.05, 0.1, and 0.5 mol) HEAs have a substantial amount of Al, which has a high affinity with the environmental oxygen above 450°C [214]. Likely, the study of the AlCoCrCuFeNiW HEAs shows a similar trend for the oxidation behavior and found that W-containing HEAs initiate oxidation at a lower temperature [190].

Moreover, the highest contents of the W in HEAs show more oxidation product (weight gain about 7%) as compared to other HEAs, indicating the formation of a more protective passive layer, which helps to protect further oxidation from occurring. It is reported [215] that W tends to forms an oxide product above 800°C. It is observed that AlCrFeMnNiW_x (x= 0.1) HEA is more stable out of all studied HEAs and offerings less oxidation over the temperature range, which is attributed to the high particle to particle diffusion during the sintering and minimize the porosity and form a high densified alloy [214]. The W-containing AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs is very stable at elevated temperature and shows improved oxidation resistance due to the formation of the passive protective oxide layer and also exhibits the outstanding melting point (as given in Table 4.1), which is more than the superalloy such as IN718 (1340°C). Therefore, the designed W-containing HEAs with improved properties could be useful as potential candidates for high-temperature applications.

4.6 Mechanical properties and density measurement of AlCrFeMnNiWx (X= 0, 0.05, 0.1, and 0.5 mol) HEA

In the present study, an Instrumented nanoindentation has been performed to evaluate the effect of the tungsten on the mechanical properties of the AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs. It is to be noted that nine random measurements are taken on the polished surface of the HEAs to ensure more reliability and repeatability of the experimental data. The Oliver and Pharr method extracted the hardness and modulus of elasticity properties from the load-displacement curve [216]. A plot between load and displacement is shown in Fig. 4.11(a), and the estimated value is presented in Fig. 4.11(b).

Initially, the studied AlCrFeMnNiW_x (x= 0) HEA shows good hardness and elastic modulus. In contrast, these properties initially decrease by the addition of the W. This is probably a reduction of phase fraction of the σ phase in the HEAs [210]. Further increase of the tungsten content

improves hardness and elastic modulus in the HEAs. However, (x=0.1) has a maximum hardness as well as elastic modulus among all HEAs. It is also seen in the previous work [217] that the atomic size difference could restrict the dislocation moment due to the local distorted and stressed crystal structure. The high hardness of the HEAs has been estimated that is possibly a combined effect of the three significant factors, such as (i) grain size strengthening, (ii) grain boundary strengthening, and (iii) precipitate hardening [218, 219]



Figure 4.9 (a) Load –displacement curve, (b) hardness and elastic modulus of AlCrFeMnNi W_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs

The instrumented hardness (H_{IT}) of the indented sample can be obtained at the peak load P_{max} by equation (4.2) [220].

Where A_p is the projected area, the relation for the evaluating elastic modulus could be expressed in equation (4.3)

$$\frac{1}{E_{\rm r}} = \frac{1 - v^2}{E_{\rm TT}} + \frac{1 - v_{\rm i}^2}{E_{\rm i}}.....(4.3)$$

Where E_r are the reduced modulus while E_{IT} , v is the elastic modulus and Poisson ratio (0.28) for the sample, respectively [221]. The modulus of elasticity E_i and Poisson ratio of the indenter v_i has also been considered in the account for the estimation of modulus. The reduced modulus has been obtained from the nanoindentation experiment according to equation (4.3) and presented in

Table 4.2. In the Table, the reduced elastic modulus and nano hardness has been presented. A small amount of the W decreases the values, but further addition of the W improves it significantly. The HEAs present an excellent combination of hardness and ductility.

| | | Nano | Elastic | Experimental | Theoretical | Relative |
|------|-----------------|------------|--------------|----------------------|----------------------|----------|
| S.No | Sample | hardness | modulus | Density | Density | Density |
| | | (GPa) | (GPa) | (g/cm ³) | (g/cm ³) | (%) |
| 1 | AlCrFeMnNi | 9.09±1.31 | 197.21±6.17 | 5.09 | 6.42 | 79.3 |
| 2 | AlCrFeMnNiW0.05 | 8.31±1.44 | 165.52±20.12 | 5.50 | 6.59 | 83.4 |
| 3 | AlCrFeMnNiW0.1 | 13.57±2.7 | 209.43±18.6 | 6.398 | 6.72 | 95.2 |
| 4 | AlCrFeMnNiW0.5 | 12.38±2.16 | 202.09±14.71 | 6.5 | 7.83 | 83 |

Table 4.2 Nano hardness, elastic modulus and densities of the AlCrFeMnNi W_x (X= 0, 0.05, 0.1,

and 0.5 mol) HEAs

The density of the AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs could be calculated by theoretical (rule of the mixture equation 2.2) and experimental (by using the Archimedes principle). A variation in the hardness and the various densities of the different HEAs has been tabulated in Table 4.3. Therefore, it is essential to note here that the W-containing spark plasma sintered HEAs having an exceptional combination of mechanical properties such as high hardness and high elastic modulus as well as high thermal stability pave the way towards the realization of developing potential high-temperature materials for structural applications.

4.7 Summary

- Nanocrystalline W-containing AlCrFeMnNi W_X (x = 0, 0.05, 0.1, 0.5 mol) HEAs have successfully synthesized through mechanical alloying cum spark plasma sintering technique.
- W-containing spark plasma sintered HEAs reveal ordered B2, BCC solid solution phase (β), FCC solid solution phase (α), and sigma phase.
- Around 95% relative density is observed in the spark plasma sintered W-containing HEAs, and the detailed sintering mechanism has been understood.
- Excellent thermal stability up to 900°C has been observed in the studied W-containing HEAs and correlated with the empirical parameters.

• The studied HEAs exhibit outstanding hardness (approx. 13.5 GPa) and modulus of elasticity (approx. 202 GPa) with the addition of tungsten, which is a signpost that the HEA is a suitable contestant for the high-temperature and wears resistance applications.

It was difficult to synthesize equiatomic AlCrFeMnNiW HEA by solidification and powder metallurgy route. However, AlCrFeMnNiW powder was prepared using mechanical alloying and its hydrogen storage capability has been reported in the next chapter.

Chapter 5

SYNTHESIS AND CHARACTERIZATION OF HYDROGENATED NOVEL AlCrFeMnNiW HIGH ENTROPY ALLOY

The high entropy alloys are the most suitable metal hydrides for high hydrogen storage capacity at room temperature. Therefore, a high entropy alloy, i.e., AlCrFeMnNiW, has been prepared, and its hydrogen storage capability study has been reported thoroughly in this section. A novel high entropy alloy (AlCrFeMnNiW) is synthesized via high-energy planetary ball milling, and the hydrogen storage behaviour of this alloy is investigated through the gravimetric method.

5.1 Phase Characterization and evidence of hydrogen absorption by XRD analysis

The XRD patterns of alloy samples are obtained by powder diffractometer using a Cu-K α radiation source at different time intervals during the ball milling process. Fig. 5.1 shows the XRD patterns of AlCrFeMnNiW HEA powders under the various ball milling duration of each 5 h interval. It can be seen that the intensity of peaks is lowered after 20 hours of milling. It may be the cause of the desolation of lower melting point elements with the highest melting point elements. Apart from that, there is no other shifting of the peak observed. The broadening of the peak is due to lattice distortion which may be due to the induced strain of excessive grain refinement by the frequent cold deformation of the powder [194]. The XRD patterns of as-prepared AlCrFeMnNiW HEA show major BCC and minor FCC phases with the lattice parameter a = 3.860 Å. Table 5.1 lists the values of lattice parameter a, unit cell volume, full width half maximum (FWHM) of most instance peak (110), the average crystallite size (D_{avg}), and d spacing of as prepared, hydrogenated, and dehydrogenated samples.



Figure 5.1 XRD patterns of equiatomic AlCrFeMnNiW HEA after different milling time

| Sample | Lattice | Unit cell | FWHM | Crystallite | d- | Peak |
|----------------|-----------|----------------------|--------|-------------|---------|---------------|
| | Parameter | Volume | (110) | Size | Spacing | (2 0) |
| | a[nm] | V [nm ³] | [deg] | (Davg)[nm] | (nm) | |
| As-prepared | 0.3152 | 0.03131 | 0.828 | 10.37 | 0.2229 | 40.412 |
| Hydrogenated | 0.3159 | 0.03152 | 0.9963 | 9.25 | 0.2234 | 40.327 |
| Dehydrogenated | 0.3157 | 0.03146 | 0.8956 | 9.87 | 0.2233 | 40.331 |

Table 5.1 Structural properties of high entropy alloy

Fig. 5.2 shows the shifting of peak (110) leftward after the alloy sample's hydrogenation and dehydrogenation. This may be due to the retained hydrogen and plastic deformation of the sample due to hydrogenation [222]. The peak (110) slightly broadened after the hydrogenation of the sample; this is due to an increase in lattice strain, which is observed to be increased from 0.0101 to 0.0114 after hydrogenation, whereas it is 0.0106 after dehydrogenation. The average crystallite size also reduced from 10.37 nm to 9.25 nm, followed by the breaking of particles. In contrast, it is also observed that the crystallite size increased to 9.87 nm after desorption of hydrogen. The crystallite sizes are evaluated by the Debye Scherrer equation, i.e., $D = \frac{0.9\lambda}{\beta cos\theta}$ where λ is wavelength of X-ray, β is line broadening at FWHM in radians and θ is Bragg's angle. On the

other hand, it can be noted that unit cell volume increased after hydrogenation and then decreased after dehydrogenation. It is evidence of hydrogenation and dehydrogenation of the sample.



Figure 5.2 XRD patterns of AlCrFeMnNiW HEA; as prepared, after hydrogenation and dehydrogenation

5.2 Dehydrogenation of HEA

AlCrFeMnNiW HEA's dehydrogenation is carried out using a Thermogravimetry instrument with the nitrogen gas environment at the flow of 60 ml/min as a protective gas. Dehydrogenation of the alloy is carried out at three different scanning rates, i.e., 5, 10, and 15 k/min, to understand desorption better.



Figure 5.3 Desorption curve of the AlCrFeMnNiW HEA at different scan rate Fig. 5.3 shows the desorption of hydrogen from HEA at different scanning rates. During dehydrogenation, the onset temperature of HEA at various heating rates, i.e., 5, 10, 15 k/min, are 60, 85, and 98.2°C, respectively. It is observed that as the temperature increases at the scan rate of 5 K/min, the mass of HEA is significantly reduced due to the release of hydrogen. It is interesting to know that when the temperature reaches 300°C, the alloy starts gaining mass due to oxidation. The oxidation of alloy occurs due to the presence of Al content [223]. The results at 10 K/min scan rate do not show significant desorption, but at 15 K/min scan rate, a similar pattern like at 5 K/min is observed, whereas reduction in HEA mass is less. Desorption of hydrogen can be easily understood from the Kissinger plot, as shown in Fig. 5. The estimated activation energy is -8.1 kJ/mol of hydrogen.

The activation energy can be calculated by the plot of 1/RT vs. ln(k) and using the following relation.

$$In(k) = \frac{E_a}{RT_p} + a....(5.1)$$

Where $K = \frac{\beta}{T_p^2} \beta$ is rate of the heating, T_p is the peak temperature, the activation energy of

desorption is E_a , R is the gas constant. The plot between In(k) and $\frac{1}{RT_p}$ is constructed whose

slope gives the value of the activation energy (E_a) as shown in Fig 5.4. Table 5.2 shows the hydrogen storage capacities of different alloys compared with the present work.



Figure 5.4 Kissinger plot for desorption of AlCrFeMnNiW HEA

| Sample | (H/M) capacity % | Temperature (°C) | Ref |
|--|------------------|------------------|--------------|
| ZrFe ₂ H _{0.12} | 0.06 | 25 | [224] |
| $Zr(Fe_{0.9}Cr_{0.1})_2H_{0.22}$ | 0.11 | 25 | [224] |
| $Zr(Fe_{0.75}Mn_{0.2})_2H_{0.45}$ | 0.22 | 25 | [18] |
| Zr(Fe _{0.8} Mn _{0.2}) ₂ H _{0.2} | 0.01 | 25 | [18] |
| $Zr(Fe_{0.9}Mn_{0.1})_2H_{0.2}$ | 0.01 | 25 | [18] |
| $Zr(Co_{0.9}V_{0.1})_2H_{0.41}$ | 0.20 | 25 | [18] |
| ZrCo ₂ H _{0.3} | 0.14 | 25 | [18] |
| CoFeMnTiVZr _{0.4} H _{0.09} | 0.03 | 25 | [18] |
| CoFeMnTiVZr _{0.7} H _{1.63} | 0.49 | 25 | [18] |
| AlCrFeMnNiW | 0.615 | 25 | Present work |

Table 5.2 Hydrogen storage capacities of different hydrogen storage alloys

5.3 Morphological approach of hydrogenated sample

The element configuration of the as-prepared alloy has been invested through the EDX analysis. Fig. 5.5 shows the EDX results of equiatomic AlCrFeMnNiW HEA. This clearly shows the homogeneous distribution of all six elements after 20 h of ball milling. The respective elements percentage is shown in Fig. 5.5.



Figure 5.5 EDX examination of as prepared AlCrFeMnNiW HEA

Figures 5.6, 5.7, and 5.8 show the Typical SEM images of as-prepared, hydrogenated, and dehydrogenated HEA samples, respectively. Fig. 5.6 shows the morphology of milled powder alloy in which regular-shaped particles can be seen after 20 h of milling due to repeated fracture of the particle inside the high energy ball mill. A small amount of very fine particles is also obtained after ball milling, which can be seen as randomly distributed black dots of different shapes. The average particle size is obtained as 10.37 nm after ball milling.

The SEM images satisfy the XRD results. The size of the particles is decreased after hydrogenation of the alloy, which results in the breaking of alloy particles into small fine particles during the absorption process. Some micro-cracks are also observed due to the penetration of the hydrogen atoms into metal surfaces. The cleave surfaces can be seen in the SEM image due to plastic deformation [225]. In Fig. 5.7, a spongy-like surface can be seen clearly. It is worth mentioning that the alloys' pulverization can be seen more during penetration of hydrogen at higher pressures [226].



Figure 5.6 Typical SEM image of as-prepared AlCrFeMnNiW HEA



Figure 5.7 Typical SEM image of hydrogenated AlCrFeMnNiW HEA


Figure 5.8 Typical SEM image of dehydrogenated AlCrFeMnNiW HEA

The hydrogenation results presented in this work are at room temperature and pressure. After desorption of hydrogen, the unit cell volume decreased due to contraction of the metal hydride, as shown in Fig. 5.8.

5.4 Summary

- A novel high entropy alloy AlCrFeMnNiW is synthesized using high-energy ball milling, and its structural and morphological properties are investigated.
- Hydrogen sorption on AlCrFeMnNiW alloy is investigated through the volumetric method, and maximum storage capacity is estimated as 0.616 wt% at room temperature and pressure with a single exposure.
- SEM analyses confirm the pulverization of the HEA particles with the presence of small micro-cracks upon hydrogenation.
- Desorption of hydrogen is carried out through TGA at different scan rates, which results in the activation energy of -8.161 KJ/mol.

Chapter 6

EFFECT OF HEAT TREATMENT ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HEAS

The desired microstructure and the properties could be achieved by suitable thermal and/or mechanical treatment. This chapter describes, the heat treatment performed on samples prepared by both arc melting and powder metallurgy routes. Consequently, the materials–process–structure–properties correlation of AlCrFeMnNiW_x (x= 0, 0.05, 0.1, and 0.5 mol) HEAs has been studied thoroughly.

6.1 Phase Analysis

XRD patterns of as-cast AlCrFeMnNiWx (x=0, 0.05, 0.1, and 0.5 mol) HEAs have been presented in Fig. 6.1. The as-cast HEAs consist mainly BCC phase, and an intense peak has been observed at near 44° (2 Θ) which corresponds to the (110) plan. After the heat treatment of 0W alloy, no phase change has been observed in the HEAs. However, a small shifting toward the higher 2 Θ side has been observed after heat treatment at 800°C. Probably, change in lattice plan due to heating at high temperature.



Figure 6.1 XRD patterns of AlCrFeMnNiWx (x= 0, 0.05, 0.1, 0.5 mol) HEAs at various Annealing temperature (a) 0W, (b) 0.05W, (c) 0.1W, and (d) 0.5W



Figure 6.2 XRD pattern of AlCrFeMnNiWx (x= 0, 0.05, 0.1, 0.5 mol) HEAs at various Annealing temperature (a) 0W, (b) 0.05W, (c) 0.1W, and (d) 0.5W

It has been observed that no other phase has been detected after 1000°C. However, an instance FCC peak has been observed in the 0.05W and 0.5W HEAs. A small peak of σ phase has been detected about 52° 2 Θ in 0.05W HEA that has not been seen in other HEAs. Generally, it has been seen that σ phase between 550 °C to 1050 °C in Cr rich alloys [227]. Evidently, the absolution of the σ phase was observed after heat treatment at 1200 °C. Formation of additional FCC phase has been found after heat treatment temperature at 800°C. Nevertheless, the formation of FCC has not been observed at the as-cast condition of the HEAs. Possibly, the FCC phase might not be detected due to very less volume fraction and nano-sized dimensions.

On the other hand, XRD patterns of spark plasma sintered HEAs after heat treatment have been present in Fig. 6. 2. the as spark plasma sintered HEAs have BCC, FCC, and σ phases initially. After the heat treatment at 800 °C, most of the peaks of σ phases has absolute and not identified in the XRD patterns. However, without tungsten-containing HEAs has a small peak of σ phases after heat treatment at 1200°C due to the high amount of Cr in the alloy system. Simultaneously,

increment of FCC phase while deduction in BCC phase has been observed. It is observed that most of the FFC diffraction peaks overlapped with the BCC peaks that is mainly due to similar lattice parameters in the XRD pattern [228].



Figure 6.3 Typical SEM images of arc melted AlCrFeMnNiWx (x=0W) HEAs at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C

6.2 Microstructure evolution study of as-cast AlCrFeMnNiW_x HEAs

The backscattered electron image (BSI) demonstrates modulated basket wave-like microstructure, and it has mainly two phases, which are dendritic (white region) and interdendritic (grey region) in as-cast HEAs [229]. During the solidification, it has been seen that the cooling rate is very high at the bottom of the sample, and it leads to the formation of columnar grains. In contrast, the upper portion that is far from the cooled bottom surface forms equiaxed grains due to the coring effect [230]. The spinodal decomposition is responsible for the microstructure. The dendritic structure is observable in the AlCrFeMnNiWx (x=0, 0.05, 0.1, and 0.5 mol) HEAs, which could be observed from the EDS data while dendritic and interdendritic has Fe-Cr rich and Al-Ni rich phase respectively [229]. Such type of tendency could be explained by all elements of the system possess a much higher melting point exclusive of Al, and they are more prospective to form a dendritic structure due to their primary solidification. The microstructure of the HEAs does not change much more after heat treatment at 800°C. It is identified that heat treatment does not change the phase

while it changes the fraction of the phases. At 1000°C of heat treatment temperature, a pronounced coarsening has been observed in the dendritic core (DC) and interdendritic (ID) regions. At 1200°C, changes entirely, in which the dendritic nature of the HEAs have been completely disappeared. The broken dendrite region could be seen in Fig. 6.3(d) that is dispersed throughout the sample. Similar behavior has been observed in all heat-treated HEAs. Differently, AMW_{0.5} HEAs that have the highest W contain represent a lamellar structure with primary BCC phase.



Figure 6.4 Typical SEM images of arc melted AlCrFeMnNiWx (x=0.05 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.5 Typical SEM images of arc melted AlCrFeMnNiWx (x=0.1 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.6 Typical SEM images of arc melted AlCrFeMnNiWx (x=0.5 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.7 EDS mapping of arc melted AlCrFeMnNiWx (X = 0, 0.05, 0.1, 0.5 mol) HEAs after heat treatment at 1200°C

6.3 Microstructure evolution of spark plasma sintered AlCrFeMnNiWx HEAs

Fig. 6.8 represents the microstructure of the spark plasma sintered samples (PMW_0) after heat treatment at 800°C, 1000°C, and 1200°C. A bright and dark grey region has been seen in the presented figures, mainly the FCC phase and AlFe type ordered phase. In addition, the sigma (σ) phase was also observed in all spark plasma sintered HEAs. The sigma (σ) phase formation mainly depends upon the amount of Cr accrual in the alloy system. The amount of the Cr also affects the formation of the sigma (σ) phase. A huge amount of Cr leads to chromium carbide, while a small amount prone to the formation of the sigma (σ) phase. The rapid diffusion of the Cr contents in the Cr rich phase is made visible in the SEM image. Evidently, the phase diagram of Cr-Fe and Cr-Ni both shown the formation of the sigma phase. Thus, Cr plays a vital role in phase formation, and it affects the microstructure, diffusion coefficient, and reaction between elements [231]. At 800°C, the phase coarsening was observed clearly in spark plasma sintered HEAs. A few porosities could be seen in the HEAs that form due to hydrostatic pressure applied at the time of sintering and diffusion of elements due to the high temperature [232]. The pronounced coarsening was observed after the heat treatment at 1000°C while Cr enriches the region (brighter) shown in the SEM images. Further heating of the sample, a significant coarsening could be observed in the HEAs at 1200°C.

In order to verify the chemical composition of the HEAs within the microstructure, EDS mapping has been carried out that is shown in Fig. 6.7 and Fig. 6.12 for the arc melted and spark plasma sintered HEAs after 1200°C respectively. It has been observed that the matrix phase rich with Mn, Cr, and Fe, while the dendritic phase rich with Al and Ni in the case of the arc melted sample. On the other hand, elemental mapping of the spark plasma sintered HEAs presents the Mn, W, and Fe homogeneous distribution except for Cr and Ni. The brighter region enriches with Cr while the grey and dark regions enrich Ni, Mn, and Fe, respectively. Thus, it is suggested that all the elements still present in the alloy system after the heat treatment.



Figure 6.8 Typical SEM images of spark plasma sintered AlCrFeMnNiWx (x=0 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.9 Typical SEM images of spark plasma sintered AlCrFeMnNiWx (x=0.05 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.10 Typical SEM images of spark plasma sintered AlCrFeMnNiWx (x=0.1 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.11 Typical SEM images of spark plasma sintered AlCrFeMnNiWx (x=0.5 W) HEA at various Annealing temperature (a) as cast, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C



Figure 6.12 EDS mapping of spark plasma sintered AlCrFeMnNiWx (X = 0, 0.05, 0.1, 0.5 mol) HEAs after heat treatment at 1200° C

6.4 Materials-structure-property correlation study

The microhardness of the arc melted and spark plasma sintered HEAs have been shown at the treated and untreated conditions in Fig. 6.13(a) In the arc melted HEAs, the value of hardness is decreasing after the heat treatment at 800°C, while increasing further except without W containing and higher W containing HEA. However, without W containing HEA represents significantly softening behavior in all temperature ranges of heat treatment. The fluctuation of different HEAs has been observed after the heat treatment, mainly due to different phases in the HEAs or lack of homogeneity of phase in the microstructure. However, AM_{0.5} HEA presents monotonous behavior due to the high amount of W presence in the alloy system. Most of W is occupied by the dendritic region, as seen in the previous study [229].



Figure 6.13 The Vickers hardness values of (a) the arc melted HEAs and (b) spark plasma sintered HEAs as a function of variation of W

Moreover, hardness values of the spark plasma sintered HEAs have shown in Fig. 6.13(b). The hardness of all HEAs decreasing significantly after heat treatment at 800°C. Additionally, further heating of HEAs increasing the hardness value except without W containing HEA. The improvement in hardness value mainly due to the existence of σ phase in the alloy system between the temperature range 550°C to 1050°C. However, the hard and brittle sigma phase's effect was not seen after the heat treatment at 800°C due to the diverse phase fraction within the HEAs.

| | As pre | pared | 80 | 0°C | 100 | 0°С | 1200°C | |
|-------|---------------|-----------------------------|---------------|-----------------------------|---------------|-----------------------------|---------------|-----------------------------|
| Alloy | Arc Melted | Spark plasma sintered | Arc Melted | Spark plasma sintered | Arc Melted | Spark plasma sintered | Arc Melted | Spark plasma sintered |
| 0W | 552 | 767 | 511 | 692 | 423 | 611 | 375 | 504 |
| 0.05W | 503 | 645 | 403 | 502 | 469 | 713 | 375 | 749 |
| 0.1W | 490 | 923 | 371 | 785 | 398 | 867 | 418 | 722 |
| 0.5W | 461 | 839 | 609 | 745 | 505 | 930 | 570 | 622 |

Table 6.1 Hardness value of different HEAs at the different heat treatment temperature

Evidently, at 1200°C, no indication has been observed of the sigma phase as X-ray diffraction suggested resultant again decrease in hardness has been estimated. It is interesting to know that the AMW₀ and PMW₀ HEAs have shown continuous softening behavior in each heat treatment temperature. The reduction in microhardness value while increasing heat treatment temperature indicates the evolution of the FCC phase and higher grain growth [233]. The Vicker hardness value is given in Table 6.1.

6.5 Summary

- Phase analysis result as a result of heat treatment
- Heat treatment effect on microstructure of as cast & spark plasma sintered samples
- Heat treatments coarsened the present phases, as expected, but also increased the amount of the FCC phase (in the spark plasma sintered sample) that makes alloy softer.
- The hardness variation has been observed due to the hard and Chromium rich sigma phase present in the HEAs that disappear after annealing at 1200°C.
- We estimated that the homogenization temperature of the investigated HEA is close to 1200°C

Chapter 7

OXIDATION BEHAVIOR OF AlCrFeMnNiW_x (x = 0, 0.05, 0.1, 0.5 mol) HIGH ENTROPY ALLOYS

In this chapter, the work demonstrates the high-temperature oxidation study of High Entropy Alloys. An extensive experiment has been performed. Initially, spark plasma sintered (SPS) AlCrFeMnNiW_x (x = 0, 0.05, 0.1, 0.5 mol) HEAs oxidized in elevated temperature at 700°C, 800°C, and 850°C isothermally and low temperature at 200°C, and 500°C in Thermal Gravimetric Analyser (TGA) for 50 hours. The HEAs exhibited multifarious behavior while adding tungsten and shows various oxides that are investigated thoroughly.

7.1 Substrate analysis

In Fig. 7.1(A), the XRD pattern of as spark plasma sintered AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEA has consist mainly BCC, FCC and chromium-rich σ phase. The effect of the addition of tungsten contents could be seen significantly in the diffraction. Initially, a small amount of the W increases the peak intensity while reducing further by introducing more W contents. An increment in peak intensity indicates the more ordered phase (AlFe type ordered BCC, JCPDS: 00-033-0020) was also observed. The reduction of the sigma phase and the FCC phase's detection have been observed simultaneously, mainly due to tungsten. Since W contents promote the BBC solid solution phase, further addition of the tungsten exposes the ordered B2 phase. Since the oxidation performance. Therefore, a line EDS has been performed on the 0.5W HEA substrate surface to understand the constituent element's distribution. In Fig. 7.1(B), an EDS line performed along with the yellow line, the Cr and Mn intensity is high throughout the surface while W is very low, stable, and uniformly distributed over the scan range.



Figure 7.1 (A) XRD pattern of the as spark plasma sintered HEAs and (B) EDS line scan of the as 0.5W HEA

7.2 Crystllographical structure and morphology of oxidized alloys at high temperature

XRD has characterized the oxidized sample's crystallographic structure at different high temperatures. The XRD revealed that multiphasic oxides had been formed over the surface. Which includes oxides, mainly Al₂O₃, Mn₂O₃, Cr₂O₃, and Mn₃O₄ with a small amount of Fe₃O₂ oxides. In Fig. 7.2 and Fig. 7.3, the XRD pattern of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs at temperature 700°C, 800°C and 850°C has been presented.

7.2.1 XRD analysis of alloys at 700°C, 800°C and 850°C

It is important to note that the alloys have behaved similarly in the case of the nature of formed oxides but entirely different in the case of the oxides' peak position at 800°C and 850°C temperatures during the XRD analysis (Fig. 7). In Fig. 7.2(B), the XRD peaks are more pronounced as compare to peaks at 700°C. A smaller number of weak peaks has been observed in the 0.05W, indicating the formation of a thick layer that dominates the small peaks. At temperatures 800°C and 850°C (in Fig. 7.2C), the alloys 0.1W and 0.5W have shown several oxides along with the evidence of the B2 matrix phase and form different discontinuous type oxides. It is worthy to note that the alloys mainly consist of Mn oxides at each temperature while Al, Cr, and Fe oxides have distributed over the entire surfaces. Interestingly, the formation of spinel structure AB_2X_4 has been observed, most similar to the MnCr₂O₄ spinel (JCPDS: 054-0876) [234].



Figure 7.2 XRD pattern of the spark plasma sintered AlCrFeMnNiWx (X= 0, 0.05, 0.1 and 0.5 mol) HEAs at (A) 700°C, (B) 800°C and (C) 850°C

7.2.2 Raman analysis of alloys at 700°C, 800°C and 850°C

Further confirmation of the formation of the oxide layers on the AlCrCuFeMnW HEAs surface was investigated through the Raman analysis. Subsequently presenting the Raman analysis for the temperature 700°C, 800°C and 850°C in the present work.

Figure 7.3 represents the Raman spectra of the oxides film formed on the alloys. At each temperature, isothermal heating of the alloy W_0 (Fig. 7.3a) exposes the small amount of the Al₂O₃ oxide, which satisfies the XRD results. At the same time, a tiny amount of Mn₂O₃ and Fe₂O₃ were also observed. It is interesting to know that the formation of Al₂O₃ oxide mainly at 800°C has been observed on all HEAs' surfaces. Also, all-alloy systems show a small amount of Cr₂O₃ and Mn₂O₃ oxides. The alloy $W_{0.5}$ has several small peaks, but only Cr₂O₃, Fe₃O₄, and Fe₂O₃ oxides have been made detected due to numerous shifting of peaks. Similarly, in higher temperature, alloy represents

also has high-intensity peaks that mean the formation of oxide is thick over the surface. At higher temperatures, most of Raman spectra have been made detected and found MnO₂, oxides.



Figure 7.3 Raman analysis of the spark plasma sintered AlCrFeMnNiWx (X= 0, 0.05, 0.1 and 0.5 mol) HEAs at (a) 700°C, (b) 800°C and (e) 850°C,

7.2.3 Morphology and chemical composition of oxides at 700°C, 800°C and 850°C The Typical SEM image analysis of the oxidized AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs has been shown in Fig. 7.4, Fig. 7.5, Fig. 7.6 at temperature 700°C, 800°C, and 850°C, respectively. The alloy consists of granular porous uniform oxides over the surface in 0W alloy at 700°C. Simultaneously, a highly magnified image presents nodule-shaped oxides, which are mainly associated with Mn oxides in Fig. 7.4(A). The EDS measurement also revealed the oxide formation with a high amount of Mn that is covered the entire sample surface. It is noted that a similar result has been observed in recently reported work by Ananiadis et al. [235]. However, a minor amount of W in the alloy does not affect more on oxide morphology, but a non-uniformed oxide has been observed in 0.05W alloy. Further addition of W contents, the 0.1W alloy has completely changed their oxide morphology. The alloy has a small faceted grain with an average size between 0.2 to 0.5 µm that is covered throughout the sample surface. Furthermore, adding W in the alloy shows a white friable grainy appearance distributed unevenly over the sample surface could be seen as an enlarged view in Fig. 7.4(D). In general, the oxide thickness grows concerning an increase in the oxidation temperature. Alloys have an oxide of Mn over the surface at 700°C, confirmed by the EDS analysis. Oxide morphology has been changed when temperature increased at 800°C that could be seen in Fig. 7.5(a & A). In alloy 0W, several large oxide particles bond together and form

a cluster along with the cracked, uneven surface. The alloy has Mn, and Al oxide and matrix elements (Fe, Cr) found in EDS spectra. The alloy 0.05W form porous oxides with Cr and Fe oxides, while the 0.1W alloy has completely uneven oxide on the sample surface. The higher amount of W-containing alloy (0.5W) presents a spherical-shaped oxide particle with a huge porous oxide surface at 800°C.

In Fig. 7.6 (a & A), fine oxide particles with regular polyhedral shapes having an average size of 3 to 5µm. Loosely packed Mn-rich spinel uniformly distributed throughout the surface at 850°C. Thus, the alloy also has oxides of Al, Fe, and Cr that the EDS detect. Alloy 0.1W showed that porous structured oxides are attached to the surface. Several inclined lines could be seen on the oxide surface that is mainly associated with the polishing direction, which was formed during the sample preparation. It has been seen that oxides of the alloy have been spalled off somewhere from the surface. The composition of the substrate has been clearly underneath the oxide layer. An irregularly shaped oxide particle with several voids has been observed in 0.5W alloy at 850°C.



Figure 7. 4 Typical SEM micrographs of oxidized AlCrFeMnNiWx {x=0 (a, A), 0.05 (b, B), 0.1 (c, C) and 0.5 (d, D)} HEAs for 50 h at 700°C



Figure 7.5 Typical SEM micrographs of oxidized AlCrFeMnNiWx {x=0 (a, A), 0.05 (b, B), 0.1 (c, C) and 0.5 (d, D)} HEAs for 50 h at 800°C



Figure 7.6 Typical SEM micrographs of oxidized AlCrFeMnNiWx {x= 0 (a, A), 0.05 (b, B) , 0.1 (c, C) and 0.5 (d, D)} HEAs for 50 h at 850°C

7.3 Crystllographical structure and morphology of oxidized alloys at Low temperature

XRD has characterized the oxidized sample's crystallographic structure at different low temperatures. The XRD revealed that multiphasic oxides had been formed over the surface during the oxidation investigation. Which includes oxides, mainly Al2O3, Mn2O3, Cr2O3, and Mn3O4 with a small amount of Fe3O2 oxides. In Fig. 7.2 and Fig. 7.3, the XRD pattern of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs at temperature 200°C, and 500°C has been presented.

7.3.1 XRD analysis of alloys at 200°C, and 500°C

At the very beginning, the alloys have shown the formation of various oxides over the surface with a high intensity of Cr oxide at 200 °C and 500 °C as shown in Fig.7.7 In Fig. 7.7(A), the XRD pattern shows the different types of mixed thin oxide. In contrast, the substrate has various phases like BCC and FCC that are not detected in the XRD in 0W alloy. The alloy has some minor peaks of Al₂O₃, Cr₂O₃, and Mn₃O₄ oxides, which are the main constituted elements of the alloy, and intensities of these peaks are very weak. Subsequently, a small amount of addition of the W in the alloy represents several weak XRD peaks of oxides. Additionally, Mn₂O₃ and Fe₃O₂ peak has been observed in the alloy. As W increases, the increment in peak intensity also increases and presents high crystallinity (in 0.1W). However, the different types of oxides are the same in nature, as found in 0.05W alloys. The XRD peak intensity has been lowered in the 0.5W alloy, signifying the thicker oxide layer. Interestingly, the evidence of discontinued type thick oxide layers has been carried out from the XRD peaks. The prominent peak has confirmed the agreement found around 65° and 82° 2Θ of ordered B2 phase, which is the main matrix of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs.



Figure 7.7 XRD pattern of the spark plasma sintered AlCrFeMnNiWx (X= 0, 0.05, 0.1 and 0.5 mol) HEAs at (A) 200°C, (B) 500°C

7.3.2 Raman analysis of alloys at 200°C and 500°C

Additional confirmation of the formation of the oxide layers at low temperature on the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs surface was examined through the Raman analysis. Afterward presenting the Raman analysis for the temperature 200°C and 500°C in the present work. Figure 7.8 represents the Raman spectra of the oxides film formed on the alloys. At each temperature, isothermal heating of the alloy W_0 (Fig. 7.8a) exposes the small amount of the Al₂O₃ oxide while Cr₂O₃ in case at 500°C, which satisfies the XRD results. At the same time, a tiny amount of Mn₂O₃ and Fe₂O₃ were also observed. It is interesting to know that the formation of Al₂O₃ oxide mainly at 200°C.



Figure 7.8 Raman analysis of the spark plasma sintered AlCrFeMnNiWx (X= 0, 0.05, 0.1 and 0.5 mol) HEAs at (a) 200°C, (b) 500°C

7.3.3 Morphology and chemical composition of oxides at 200°C and 500°C

The Typical SEM analysis of the oxidized AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs has been shown in Fig. 7.9, and Fig. 7.10 at temperature 200°C and 500°C, respectively. At the beginning of the oxidation at 200°C and 500°C, the alloy shows a small amount of the oxides in SEM images. It is seen that the oxides have been taken place in the grain boundary region due to high energy sites in this area. It is also seen that the oxides are aligned with the polishing direction, which is mainly due to the sufficient amount of oxygen present in those areas. It has been seen that 0.1W alloys demonstrate a granular morphology at 200°C and 500°C near the grain boundary, while small spherical oxides (~ 1-2 μ) are seen throughout the surface in 0.5W HEAs.



Figure 7.9 Typical SEM micrographs of oxidized AlCrFeMnNiWx {x= 0 (a, A), 0.05 (b, B), 0.1 (c, C) and 0.5 (d, D)} HEAs for 50 h at 200°C



Figure 7.10 Typical SEM micrographs of oxidized AlCrFeMnNiWx {x=0 (a, A), 0.05 (b, B), 0.1 (c, C) and 0.5 (d, D)} HEAs for 50 h at 500°C

7.4 Oxidation kinetics

The oxidation behavior of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs has been investigated at the temperature 200°C, 500°C, 700°C, 800°C and 850°C. The recorded investigation of the TGA instrument has been plotted as a function of oxidation time and mass gain per unit area for better understanding, whereas temperature has been isothermal. The oxidation of the alloy at a high temperature usually obeys the parabolic law. Here, most of them alloys have followed the parabolic rate law. Thus the parabolic law [236] could be express as

$$\left(\frac{\Delta W}{A}\right)^2 = \mathbf{K}_p t....(7.1)$$

Kp is the parabolic rate constant, ΔW , and t is the change in mass per unit area of sample and exposer time. Fig. 7.11 and Fig. 7.12 represented thermogravimetry graph of the AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs for 50 h oxidation at different temperatures. All alloys exhibit a rapid mass change in the initial hour of the oxidation as the classical oxidation curve is formed [237].

The alloys at a lower temperature, i.e., 200°C and 500°C, have represented a good oxidation behavior. Negligible, the significantly less mass gain has been observed at 200°C except 0.05W HEA in Fig. 7.11(a). Alloys of 0.1W and 0.5W show an excellent oxidation resistance at 500°C while 0W and 0.05W HEAs have presented a 2% to 5% mass gain at the temperature (Fig. 7.11b). The alloy without contenting W (0W alloy) exhibits resistive behavior against 700°C and presents minor oxidation during the oxidation period compared to other alloys. However, 0.5W alloy present maximum oxidation, and alloy shows a slow reduction in the oxidation rate recorded at the end of the oxidation. Out of all them, 0.05W and 0.1W alloy has attained mass gain ~ 4mg/cm² in which 0.05W alloy follows the same trend as 0.5W alloy with less mass gain. As the oxidation temperature increases, the alloy's behavior also changed, as seen in Fig. (B) at 800°C. The 0.05 alloy followed the parabolic rate law while the other alloy did not follow the parabolic rate law perfectly.

Nevertheless, the remaining three alloys, 0W, 0.1W, and 0.5W, have shown similar trends with significantly less mass gain at 800°C. The highest oxidation temperature, 850°C of the present study, shows entirely different alloy trends. The without W containing (0W) and maximum (0.5W) alloy has affected much more at a given temperature. It shows ~ 4.5 mg/cm^2 mass gain during the oxidation period. However, all high entropy alloys have shown more than 1.5 mg/cm² within the

first 2 hours. Later, all HEAs presents typical behavior, and none of them followed neither parabolic nor linear rate law perfectly. Herein, there are a few pieces of evidence found for the cracking or spallation of the oxides.



Figure 7.11 Oxidation kinetics of AlCrFeMnNiWx (X= 0, 0.05, 0.1, and 0.5 mol) HEAs at (a) 200°C, and (b) 500°C

Table 7.1 The values of oxidation rate constant (K_p) and activation energy (Q) of

| K _p values gm ² /cm ⁴ - sec | | | | | | | | | | |
|--|--------------------------|--------------------------|--------------------------|------------|-------|--|--|--|--|--|
| Тетр | 700°C | 800°C | 850°C | Activation | Ref. | | | | | |
| Allovs | | | | Energy Q | | | | | | |
| | | | | (KJ/mol) | | | | | | |
| AlCrFeMnNiW ₀ | 2.266X10 ⁻¹¹ | 5.866 X10 ⁻¹⁰ | 6.919 X10 ⁻¹⁰ | 220.27 | * | | | | | |
| AlCrFeMnNiW0.05 | 1.283 X10 ⁻¹⁰ | 4.398 X10 ⁻⁹ | 1.468 X10 ⁻¹⁰ | 21.0 | * | | | | | |
| AlCrFeMnNiW _{0.1} | 1.297X10 ⁻¹⁰ | 1.37 X10 ⁻¹⁰ | 1.365 X10 ⁻¹⁰ | 49.02 | * | | | | | |
| AlCrFeMnNiW _{0.5} | 4.176 X10 ⁻¹⁰ | 3.04 X10 ⁻¹⁰ | 8.550 X10 ⁻¹⁰ | 83.56 | * | | | | | |
| FeCoNiCrAl | 2.6 X10 ⁻¹⁵ | 4 X10 ⁻¹⁴ | - | 226.2 | [238] | | | | | |
| FeCoNiCrMn | 5.1 X10 ⁻¹² | 1.5 X10 ⁻¹¹ | 2.2 X10 ⁻¹¹ | 109 | [238] | | | | | |
| FeCoNiCrSi | 5.1 X10 ⁻¹⁴ | 1.8 X10 ⁻¹³ | - | 145.5 | [238] | | | | | |
| Al0.1CoCrFeNi | 1.61 X10-12 | 4.83 X10-11 | - | - | [239] | | | | | |
| CoCrCuFeNiSi0 | 1.73 X10 ⁻¹⁰ | 1.80 X10 ⁻¹⁰ | - | - | [126] | | | | | |

| CoCrCuFeNiSi0.3 | 1.88 X10 ⁻¹⁰ | 1.97X10 ⁻¹⁰ | - | - | [126] | | | | |
|-----------------|-------------------------|-------------------------|---|---|-------|--|--|--|--|
| CoCrCuFeNiSi0.6 | 1.27 X10 ⁻¹⁰ | 1.65 X10 ⁻¹⁰ | - | - | [126] | | | | |
| Rene95 Ni-based | | 9.184×10^{-13} | - | - | [240] | | | | |
| superalloy | | | | | | | | | |
| * Present study | | | | | | | | | |



Figure 7.12 Oxidation kinetics of AlCrFeMnNiWx (X= 0, 0.05, 0.1, and 0.5 mol) HEAs at (A)700°C, (B) 800°C and (C) 850°C

The oxidation behavior could be more understandable when the K_p value is calculated by using equation (7.1). In Table 7.1, the K_p values and activation energy of the alloys have been estimated at different temperatures as well as a comparison also made with reported alloys. Higher

temperatures showed more oxidation rates in most alloys in the table compared to lower temperatures.

7.5 Discussion

The present work emphasized to understand the oxidation behavior of the AlCrFeMnNiWx (x=0, 0.05, 0.1, 0.5 mol) HEAs at high temperature. Moreover, to develop an informative model by using the ANN to predict mass gain at high-temperature oxidation. The section first describes the results obtained by various characterizations and understands the oxidation mechanism due to the W in the HEA alloy.

As seen in Fig. 7.2, the XRD characterized the different types of multiphasic oxide on all HEAs. However, Mn oxides have been seen in most of the alloys. The oxidation of the elements starts i.e. Al>300°C [60], Cr>400°C [126, 241], Mn>300°C [242], Ni>500°C [126, 241], Fe>700°C [126, 241], W>400°C [241]. Thus, Mn and Al are most likely to form oxide products first. Based on some fundamental knowledge of multicomponent alloy that has been reported in previous work, before steady-state conditions of oxidation, a transient oxidation state has been seen in the initial few hours. In this short period, the immediate consumption of oxygen has been observed, leading to localized, non-uniform oxides, including spinel. Hence, oxidation behavior has been affected entirely at the beginning of the oxidation [243]. In Fig. 7.11, the transient state of oxidation of the HEAs could be seen at the initial 2-3 hours. In the oxidation of AlCrFeMnNiW_x (x= 0, 0.05, 0.1, 0.5 mol) HEAs, the interfacial reaction played a great role at the beginning of the oxidation. In this stage, the conversion of the alloy surface into the oxide layer has been assumed owing to the faster consumption of the oxygen.

Furthermore, the diffusion process has been taking place to influence the reaction. Since the initial oxide layer is formed over the alloy surfaces, oxygen activity is not sufficient; thus, oxygen starts to penetrate the alloy substrate through oxides. In Mn-rich alloys, It has been reported that the Mn diffused faster than the Cr to form the external oxide scale [244]. It is also known that oxygen activity for oxidized Al is lesser than the oxidized Cr. Thus, the formation of Al oxides could be considered in further stages and Cr oxide in a later stage. According to the Ellingham diagram, the Gibbs free energies are at a temperature of interest is $\Delta G^{\theta}_{Al_2O_3} < \Delta G^{\theta}_{Cr_2O_3} < \Delta G^{\theta}_{MnO_2}$ [243]. That means all oxidation reaction of metal elements in the AlCrFeMnNiW_x (x= 0, 0.05, 0.1, 0.5 mol) HEAs is proceed spontaneously. Thus, the lower Gibbs free energy means better affinity with oxygen [245]. Hence, Al₂O₃ is the most stable oxide among

all of them. In the meantime, the diffusion of the Fe anion occurred and formed discontinuous Fe oxide.

In conventional Mn alloys, the possibilities of the presence of spinels have been seen widely, which has less protective Mn-containing spinels. However, a small amount of Mn shows the contrary effect in Fe-Cr binary alloys for the oxidation resistance. The formation of less protective MnCr₂O₄ spinel has the only reason for the adverse effect. It is also reported that the oxidation rate is higher in such cases where MnCr₂O₄ spinel formed because Mn facilitated to form scaled blistering and cracking of oxide layers [235, 246–248]. In the case of AlCrFeMnNiWx (x= 0, 0.05, 0.1, 0.5 mol) HEAs, the possible spinel MnCr₂O₄ has been assumed because Mn could exist as a form of MnCr₂O₄ spinel in the Cr₂O₃ matrix [244]. Simultaneously, there is no evidence found in the XRD analysis, but the SEM micrograph clearly showed the Mn-rich spinel in maximum Mn containing HEA (0W) at 850°C. A schematic illustration has been proposed in Fig. 7.13 that shows the oxidation mechanism with and without tungsten-containing HEAs. The possible reaction of formation of the spinel is shown in equation (7.2)

$$MnO(s)+Cr_2O_3(s) \rightarrow MnCr_2O_4(s) \dots (7.2)$$

To design a HEA for a high-temperature application, activation energy on diffusion has played a crucial role. Hence In Table 7.2, the activation energy has been evaluated by the Arrhenius equation. In contrast, the equimolar alloy (0W) has presented the highest activation energy (Q = 220.27 KJ/mol) out of studied HEAs, which is higher than T-19 steel [249] and slightly lower from Ni-based superalloys [250]. The equimolar HEA has high configurational entropy that promotes the potential need for atomic motion due to atomic variability. Accordingly, the free energy, which is acts as a driving force for the reaction, would be small in these HEA that lowers the diffusion of the metal atoms by restricting the migration from one site to another site if it is trapped in lower potential sites. Thus, a slowing down of the diffusion process occurred [239]. The HEA after the addition of the tungsten has presented a higher oxidation rate as compared to without tungsten added HEA at 700°C. By adding the high atomic radius elements in the AlCrFeMnNi HEA, the severe lattice distortion comes up with the action in the oxidation process. Recently, wang et al. presents their work, which is based on the effect of lattice distortion on the diffusion behavior of TiZrNbTa HEA. All the constituent elements of the HEA have a higher atomic radius as compared to traditional alloying elements. The work significantly presents the severe lattice

distortion, and more dislocation in TiZr rich regions conducts higher diffusion of the oxygen atom and oxidation rate [53].

In contrast, if the generation of dislocation pipe is inadequate due to the desired limit of the threshold, it slows down the oxygen diffusion. The lattice distortion may be a probable reason for the high oxidation in the tungsten added HEAs. Monotonically oxidation behavior has been seen in 0.05W HEA at 800°C, while relatively low oxidation has been seen at 850°C. All of those, the higher W content (above 3.59 wt %) improves the oxidation resistance and keeping the oxidation limited up to $\Delta w = 5 \text{ mg/cm}^2$ in the oxidation period. The addition of the tungsten promotes the formation of Cr₂O₃ at a lower concentration of chromium and acts as a barrier for inward oxygen flux that leads the better oxidation resistance. Evidently, in Table 7.2, improvement in activation energy has been occurred progressively by the addition of tungsten.



Figure 7.13 Oxidation mechanism of the HEAs

A similar result has been seen in Gao's work, whereas up to 25 wt% of W improves the oxidation resistance by restricting inward oxygen flux. Additionally, above 25 wt% of W, a detrimental effect that prevents creating the protective layer and formation of NiWO₄ leads to cracking of the protective layer near the metal scale interface [251]. Nevertheless, the evidence of the formation of the NiWO₄ scale has not been seen in the study, while the 0.5W alloy has 26.8 wt% tungsten contents.

7.6 Summary

• The low temperature oxidation of AlCrFeMnNiW_X (x = 0, 0.05, 0.1, 0.5 mol) HEAs presents parabolic oxidation kinetic and excellent oxidation resistant has been observed in

most of HEAs. The HEAs present the linear and parabolic kinetics behavior in the investigation period.

- W (up to 3.59 wt%) promotes the oxide formation at 700°C while further adding W limiting (up to $\Delta w = 5 \text{mg/cm}^2$) the oxide formation except for 0.05W alloy at 800°C.
- Rapid consumption of the oxygen has been seen in the transient oxidation state at the initial 2-3 hr of oxidation that formed localized and non-uniform oxides. After that, multiphasic oxides were formed concerning constituent elements of HEAs at a further stage.

Chapter 8

ARTIFICIAL NEURAL NETWORK APPROACH FOR PROPERTIES PREDICTION IN HEAs

The experimental investigation is a conventional technique in which the exact and reliable results could be found. However, where time and material have an essential concern for the researcher. Simulation and modeling are some of the best techniques to avoid uncertainty and delay due to the experiment. There are several computation methods to predict accurate results based on previous experience of experimental work, such as Artificial Neural Network (ANN) [229], which is worked as the human brain [252, 253]. Artificial Intelligence (AI) has been established for the development of production software that enables complex and intelligent computation like human brains. That includes tools, methods, and reasoning activity for solving complex problems. AI categorically works a model as a brain work i. e. Artificial Neural Network(ANN) [254]. An ANN can be understood as a modeling technique that is most similar to the human brain. It is a highly interconnected structure that is parallelly distributed in process units. The network is having a large number of simple processing units called neurons, also known as Processing Elements (PE), which makes possible the receiving, processing, and transmitting the information in the term of computer science. Each neuron has its weight when connected to different neurons. The association between neurons to a significant amount chooses the working of the system. A component that includes the subgroups called layer [255]. The system is structured with three layers, i.e., an input layer, a hidden layer, and an output layer, which work as input fed in the model for the processing of the information received from the input layer and to make available to the output layer after processing respectively.

Recently, Kim et al. have proposed their work in which regression analysis has been performed to oxidate Ni-based superalloy using the ANN technique. An excellent regression result has been drawn that suggested the optimal composition of the alloy [256]. In this computational technique, initially experimented data has fed in the form of input data, and output data has been received after processing the input. The technique is extensively used to predict the mechanical properties [199, 257, 258] and the material's behavior in the material science communities [259].

8.1 Use of the Artificial Neural Network for hardness prediction in spark plasma sintered sample

8.1.1 Collection of the dataset and framework

The assortment of the HEAs hardness dataset for the present work has been chosen from the various previous reported articles, which is based on the experimental work. It is to be noted that the composition of each HEA is taken in the weight percentage. All the HEAs were prepared by the spark plasma sintering (SPS) technique used as a dataset for hardness. The 32 HEAs have been collected from previously reported work, and 4 HEAs were used from the present work for making the dataset. The combination of the all-type hardness range and sintering temperature has been chosen for the work. Subsequently, Fig. 8.1 represents the numbers of selected HEAs against their hardness. The elemental composition and hardness of the HEAs have been taken in Wt.% and HV (Vickers Hardness), respectively (as shown in Table 8.1).



Figure 8.1 No of HEAs concerning hardness distribution used in the work

The details of the framework are given in Fig. 8.2. The schematic path of the complete experimental and modeling procedure of the present study is highlighted. An appropriate backpropagation ANN model has been developed based on several trials for numbers of neurons. The adjusting number of hidden layers has been optimized by the training, validation, and testing. Further, the output results of the model have been compared with the actual values of hardness. The absolute value has been calculated by the difference between the predicted value and the exact value. The model has been trained and tested until the expected limit of error is not met for the best predictive value of hardness.

Table 8.1 Prepared data set including elemental composition (wt.%), sintering temperature (°C), and hardness (HV) of different HEAs

| Al | | | Cu | Fe | Mn | Ni | W | Temp °C | Exp | |
|------|-------|-------|-------|-------|-------|-------|---|------------|----------|-----------|
| | Со | Cr | | | | | | | Hardness | Reference |
| | | | | | | | | C | (HV) | |
| 0 | 17.8 | 18.5 | 0 | 23.96 | 20.33 | 19.41 | 0 | 800 | 352 | [260] |
| 0 | 17.8 | 18.5 | 0 | 23.96 | 20.33 | 19.41 | 0 | 1000 | 424 | [260] |
| 8.78 | 19.17 | 16.92 | 0 | 18.17 | 17.87 | 19.09 | 0 | 800 | 662 | [261] |
| 0 | 33.99 | 0 | 0 | 32.18 | 0 | 33.82 | 0 | 800 | 380 | [262] |
| 0 | 26.14 | 23.06 | 0 | 24.77 | 0 | 26.03 | 0 | 800 | 400 | [262] |
| 0 | 26.14 | 23.06 | 0 | 24.77 | 0 | 26.03 | 0 | 900 | 570 | [262] |
| 0 | 26.14 | 23.06 | 0 | 24.77 | 0 | 26.03 | 0 | 1000 | 590 | [262] |
| 0 | 24.86 | 0 | 26.81 | 23.56 | 0 | 24.76 | 0 | 700 | 385 | [262] |
| 0 | 24.86 | 0 | 26.81 | 23.56 | 0 | 24.76 | 0 | 800 | 340 | [262] |
| 0 | 24.86 | 0 | 26.81 | 23.56 | 0 | 24.76 | 0 | 900 | 330 | [262] |
| 0 | 25.8 | 0 | 0 | 24.45 | 24.05 | 25.7 | 0 | 800 | 500 | [262] |
| 0 | 25.8 | 0 | 0 | 24.45 | 24.05 | 25.7 | 0 | 900 | 460 | [262] |
| 0 | 25.8 | 0 | 0 | 24.45 | 24.05 | 25.7 | 0 | 1000 | 350 | [262] |
| 0 | 26.14 | 23.06 | 0 | 24.77 | 0 | 26.03 | 0 | 900 | 570 | [263] |
| 0 | 21.02 | 18.54 | 0 | 19.92 | 19.59 | 20.93 | 0 | 800 | 646 | [264] |

| 6.69 | 24.39 | 21.52 | 0 | 23.11 | 0 | 24.29 | 0 | 1000 | 594 | [265] |
|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|---------|
| 7.49 | 0 | 28.88 | 0 | 31.02 | 0 | 32.6 | 0 | 1000 | 552 | [265] |
| 10.49 | 22.9 | 20.21 | 24.7 | 21.7 | 0 | 0 | 0 | 900 | 770 | [15] |
| 0 | 20.39 | 17.99 | 21.99 | 19.32 | 0 | 20.31 | 0 | 900 | 400 | [15] |
| 0 | 26.14 | 23.06 | 0 | 24.77 | 0 | 26.03 | 0 | 900 | 490 | [15] |
| 13.6 | 0 | 26.21 | 32.03 | 28.15 | 0 | 0 | 0 | 800 | 650 | [17] |
| 9.3 | 8.7 | 25.6 | 0 | 27.5 | 0 | 28.9 | 0 | 1000 | 624 | [227] |
| 10.65 | 0 | 20.53 | 25.09 | 22.05 | 21.69 | 0 | 0 | 900 | 633 | [19] |
| 10.28 | 0 | 19.81 | 24.21 | 21.27 | 20.93 | 0 | 3.5 | 900 | 680 | [19] |
| 9.93 | 0 | 19.14 | 23.39 | 20.56 | 20.43 | 0 | 6.56 | 900 | 705 | [19] |
| 7.84 | 0 | 15.11 | 18.46 | 16.22 | 15.96 | 0 | 26.41 | 900 | 780 | [19] |
| 6.17 | 0 | 11.89 | 14.54 | 12.77 | 12.57 | 0 | 42.06 | 900 | 891.5 | [19] |
| 10.86 | 0 | 20.93 | 0 | 22.48 | 22.11 | 23.62 | 0 | 900 | 753* | present |
| | | | | | | | | | | work |
| 10.47 | 0 | 20.18 | 0 | 21.68 | 21.32 | 22.78 | 3.57 | 900 | 644* | present |
| | | | | | | | | | | work |
| 10.13 | 0 | 19.53 | 0 | 20.97 | 20.63 | 22.04 | 6.69 | 900 | 923* | present |
| | | | | | | | | | | work |
| 7.95 | 0 | 15.32 | 0 | 16.46 | 16.19 | 17.29 | 26.79 | 900 | 839* | present |
| | _ | | - | | | | | | | work |
| 2.59 | 22.87 | 16.84 | 20.59 | 18.09 | 0 | 19.01 | 0 | 1050 | 645 | [266] |
| 10.5 | 0 | 20.23 | 24.72 | 21.72 | 0 | 22.83 | 0 | 700 | 443 | [267] |
| 10.5 | 0 | 20.23 | 24.72 | 21.72 | 0 | 22.83 | 0 | 800 | 704 | [267] |
| 10.5 | 0 | 20.23 | 24.72 | 21.72 | 0 | 22.83 | 0 | 800 | 851 | [267] |
| 10.5 | 0 | 20.23 | 24.72 | 21.72 | 0 | 22.83 | 0 | 900 | 879 | [267] |



Figure 8.2 Schematic representation of framework for the study

8.1.2 Modeling details

In general, the ANN model having three different layers named input, hidden, and output layers. Every layer has a specific component called neurons connected. The neurons' communication signal is accomplished with the linking weight, and each neuron's input passes numerous inputs from previous neurons to adjust the weight. Eventually, the output has been calculated by the model after several iterations. A backpropagation is the most suitable and popular algorithm for predicting the properties for material modeling. Thus, A backpropagation artificial neural network has been utilized better to understand the relationship between input and output datasets. A model with a 9-9-1 structure (9 neurons in the input layer, 9 neurons in the hidden layer, and 1 neuron in the output layer) has been employed. The elemental composition of Al, Co, Cr, Cu, Mn, Ni, Fe, W, and the sintering temperature has been considered as an input parameter. The composition of individual elements is in atomic percentage and the sintering temperature in degree centigrade. At the same time, the hardness of the sintered HEAs is an output parameter for the model. The MATLAB 9.6 (R2019a) was used for the implementation of the model. Out of 34 datasets, training
(15%), validation (15%), and testing (70%) have been performed. Fig. 8.3 presents the proposed backpropagation artificial neural network model for the present study.



Figure 8.3 proposed a generalized model for the present work

8.1.3 Training, Testing, and Validation of the ANN model

A backpropagation neural network has been applied to the model, which predicts the hardness of the alloys. Initially, all dataset has been scaled by the feature scaling function to maintain the steadiness of the input dataset. The generalized equation of feature scaling is given in equation (8.1) [268]. A set of 36 data has been divided into three parts for training, validation, and testing to build the model, which is 70%, 15%, and 15%, respectively. A neural network structure 9-9-1 has been selected to implement the model by applying the error and trial method. The Levenberg Marquardt training algorithm has been used to train the ANN model. During the ANN model implementation, MSE between predicted and desire output has also been calculated, which is equal to the 0.18468 (as shown in Fig. 8.4), which is saturated in five epochs.



Figure 8.4 MSE convergence of the ANN model for best validation performance

8.1.4 predictive results of Backpropagation ANN model for hardness

In order to develop a generalized model for the combined effect of the HEA containing Al, Cr, Co, Cu, Mn, Fe, Ni, W elements, and sintering temperature, which influences the hardness of the alloy. After several iterations and re-training of the ANN model, an excellent correlation coefficient was attained for the training, validation, and testing, which is R=0.981, R=0.976 R=0.982, respectively. However, the overall AlCuCoNiMnFeCrW alloy best test set R=0.971 has been estimated and is presented in Fig. 8.5(i). The ANN model provides an error of 4.05% and an accuracy of 95.95% in the predicted value, which is an outstanding agreement between the predicted and experimental results. It is observed that the prediction of hardness with less accuracy of some data points is expected. The possible reason is that the HEAs were processed via the SPS technique, and It has a different amount of porosity that is not always mentioned in the reported literature. Sometimes the densification significantly affects the hardness value. The study has a collection of such experimental hardness with the same alloying composition and same processing route that is limited available in the literature. Thus the predicted model is slightly underfitting [269]. However, the model's accuracy is quite good enough to predict the hardness value. The details of the experimental and predicted values are given in Table 8.2 and are also represented in a graphical view shown in Fig. 8.5(ii). It is worthy of mentioning that the developed ANN model predicts the suitable HEA composition with desired mechanical properties by avoiding many experimental trials, and hence, the designed HEAs can be considered as potential candidates for specific applications.



Figure 8.5 (i) Presentation of correlation between the experimental and predicted hardness (ii) comparison of the experimental and ANN predicted hardness

| sample | Exp Hardness | ANN Hardness | Absolute error % | Accuracy% |
|--------|--------------|--------------|------------------|-----------|
| 1 | 352 | 340.01 | 3.41 | 96.59 |
| 2 | 424 | 422.74 | 0.30 | 99.70 |
| 3 | 662 | 658.69 | 0.50 | 99.50 |
| 4 | 380 | 338.00 | 11.05 | 88.95 |
| 5 | 400 | 399.43 | 0.14 | 99.86 |
| 6 | 570 | 529.65 | 7.08 | 92.92 |
| 7 | 590 | 588.11 | 0.32 | 99.68 |
| 8 | 385 | 390.93 | 1.54 | 98.46 |
| 9 | 340 | 359.38 | 5.70 | 94.30 |
| 10 | 330 | 348.46 | 5.60 | 94.40 |
| 11 | 500 | 508.86 | 1.77 | 98.23 |
| 12 | 460 | 454.32 | 1.23 | 98.77 |
| 13 | 350 | 355.18 | 1.48 | 98.52 |
| 14 | 570 | 529.65 | 7.08 | 92.92 |

Table 8.2 Comparison of Experimental and Predicted hardness calculated by ANN model

| 15 | 646 | 632.90 | 2.03 | 97.97 |
|---------|-------|--------|-------|--------|
| 16 | 594 | 601.86 | 1.32 | 98.68 |
| 17 | 552 | 557.82 | 1.05 | 98.95 |
| 18 | 770 | 773.99 | 0.52 | 99.48 |
| 19 | 400 | 410.17 | 2.54 | 97.46 |
| 20 | 490 | 529.65 | 8.09 | 91.91 |
| 21 | 650 | 645.69 | 0.66 | 99.34 |
| 22 | 624 | 628.69 | 0.75 | 99.25 |
| 23 | 633 | 627.38 | 0.89 | 99.11 |
| 24 | 680 | 650.12 | 4.39 | 95.61 |
| 25 | 705 | 668.86 | 5.13 | 94.87 |
| 26 | 780 | 803.35 | 2.99 | 97.01 |
| 27 | 891.5 | 867.82 | 2.66 | 97.34 |
| 28 | 753 | 668.37 | 11.24 | 88.76 |
| 29 | 644 | 735.34 | 14.18 | 85.82 |
| 30 | 923 | 790.23 | 14.38 | 85.62 |
| 31 | 839 | 864.83 | 3.08 | 96.92 |
| 32 | 645 | 654.61 | 1.49 | 98.51 |
| 33 | 443 | 458.09 | 3.41 | 96.59 |
| 34 | 704 | 718.21 | 2.02 | 97.98 |
| 35 | 851 | 718.21 | 15.60 | 84.40 |
| 36 | 879 | 877.59 | 0.16 | 99.84 |
| Average | | | 4.049 | 95.950 |

8.2 Use of Artificial Neural Network for mass gain in high-temperature oxidation

8.2.1 Interpretation of Oxidation kinetics law

It has been observed that several researchers have shown the quantification of the oxidation kinetic by basic physical models, which are parabolic, linear, and logarithmic law [237]. However, the parabolic and linear laws are used in most of the oxidized alloys to finding the oxidation rate constant. It is also seen that the combination of these laws employed some time to study oxidation

kinetics [123]. Nevertheless, using a physical model for the oxidation study would sometimes not provide accurate results. The study has been done based on the fitting of experimental data, which is associated with the basic physical model. The accuracy of the K_p value depends upon the selection of oxidation law, which is being followed by the experimental oxidation curve. The present study also has the same problem and then makes more effort to overcome it. In Fig. 8.6, the oxidation curve has been fitted with different physical models that these basic physical models could not adequately fit. However, some of them fitted well but remaining curve has not fitted even up to a satisfactory in case of parabolic as well as linear fitting. The calculated values of coefficient of determination (\mathbb{R}^2) obtained from the regression analysis of different oxidation curves have been given in Table 8.3.

| 0.5 mol) HEAs at 700°C, 800°C and 850°C | | | | | | |
|---|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
| Тетр | 70 | 700°C 800°C | | 0°C | 850°C | |
| Alloys | Linear | Parabolic | Linear | Parabolic | Linear | Parabolic |
| | law (\mathbb{R}^2) | law (R ²) | law (\mathbb{R}^2) | law (R ²) | law (\mathbb{R}^2) | law (R ²) |
| AlCrFeMnNiW ₀ | 0.82 | 0.96 | 0.51 | 0.95 | 0.91 | 0.99 |
| AlCrFeMnNiW0.05 | 0.19 | 0.65 | 0.85 | 0.99 | 0.71 | 0.92 |
| AlCrFeMnNiW _{0.1} | 0.91 | 0.98 | 0.84 | 0.66 | 0.89 | 0.93 |
| AlCrFeMnNiW _{0.5} | 0.30 | 0.71 | 0.82 | 0.91 | 0.98 | 0.99 |

| Table 8.3 The va | alues of oxidation | rate constant (K _I | p) of AlCrFeMnN | iWx (X=0, 0.05 | 5, 0.1, and |
|------------------|--------------------|-------------------------------|-----------------|----------------|-------------|
| | | | | | |

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Figure 8.6 Oxidation curve with fitting by parabolic law (A, B, C) and linear law (D, E, F) of AlCrFeMnNiWx (X= 0, 0.05, 0.1, and 0.5 mol) HEAs at (A)700°C, (B) 800°C and (C) 850°C

As shown in Fig. 8.6, the mass gain of the AlCrFeMnNiWx (X=0, 0.05, 0.1, and 0.5 mol) HEAs at different oxidation temperatures could not determine accurately. However, the problem would be minimized by using a suitable prediction model. The accurate prediction of mass gain could be estimated if the model results completely satisfied the experiment results accurately, such as ANN are used.

8.2.2 ANN model results

A backpropagation model can simulate the data set given as input and predict the mass gain at high-temperature oxidation. Thus, the 8-13-1 model has been selected after several trials. The model has been selected based on MSE (Mean Square Error), which is the most critical factor for accurate prediction results. However, most of the trials had given good predictions, but the best result has been chosen for the study.

| | Mean Square Error (MSE) | | | |
|--------------------------|-------------------------|---------|--|--|
| Network structure | Training | Testing | | |
| 8-11-1 | 0.0188 | 0.0195 | | |
| 8-12-1 | 0.0135 | 0.0138 | | |
| 8-13-1* | 0.0095 | 0.0104 | | |
| 8-14-1 | 0.0128 | 0.0161 | | |
| 8-15-1 | 0.0199 | 0.0192 | | |
| * Proposed model for thi | s study | | | |

Table 8.4 MSE comparison of different ANN structure

Table 8.4 shows that the MSE of different ANN structures has been used to evaluate the best results model. In order to achieve the best result, the 8-13-1 structure has been selected according to the most negligible MSE value. ANN model 8-13-1 has shown the best validation performance 9.0353X10⁻³ after 1000 epochs in Fig. 8.7(A), while the effect of MSE concerning the number of hidden layers in Fig. 8.7(B).



Figure 8.7 (A) best validation performance, and (B) no of hidden layers concerning MSE of selected 8-13-1 ANN model

The ANN predictive model's obtained result could be compared with the experiment data and plot to understand how close the data. Hence, Fig. 8.8 represented a comparison between the experiment and the predicted results. The predicted results are very close to the experimental result, where the R-value of training, testing, and validation are 0.9997, 0.9996, and 0.9997, respectively. Thus, the predictive result is accurate enough to predict the mass gain in further stages using the 8-13-1 ANN model.



Figure 8.8 Comparison of experimental and predicted (ANN) results for mass gain



Figure 8.9 Mass change per unit area of AlCrFeMnNiWx (x= 0, 0.05, 0.1, and 0.5 mol) HEAs with ANN prediction at (A)700°C, (B) 800°C and (C) 850°C

Eventually, the ANN model results have been plotted along with the experimental data and found that the mass gain prediction is precisely the same as experimental findings. Fig. 8.9 exhibits that the predicted mass gain is very close to the experimental curve, which shows the ANN model's applicability for predicting the oxidation kinetics of AlCrFeMnNiWx (x=0, 0.05, 0.1, and 0.5 mol) HEAs at 700°C, 800°C, and 850°C. It also noted that the ANN model is an accurate and reliable technique to predict oxidation kinetics.

8.4 Summary

• An excellent correlation has been estimated by the developed ANN model using the alloying composition, sintering temperature, and hardness of the spark plasma sintered AlCrFeMnNiWx (x= 0, 0.05, 0.1, and 0.5 mol) HEAs.

- Successfully Applied the predictive backpropagation ANN model in the case of oxidation study, which enlightened the excellent agreement with experimental data.
- The ANN model demonstrated the precise prediction of mass gain value compared to the physical model confirms that the ANN is a powerful tool for modeling and analysis, which could be used for process and product design.

Chapter 9

CONCLUSIONS

The following conclusions may be summarized based on present research work

- The multicomponent AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs are successfully developed via arc melting and powder metallurgy route.
- The multicomponent AlCrFeMnNiWx (x = 0, 0.05, 0.1, 0.5 mol) HEAs are developed using integrated approach of combining thermodynamic simulation and experimental method. SEM and XRD results reveal the formation of the BCC Fe-Cr-Mn rich (β1) primary phase and BCC Ni-Al-rich phase (β2) interdendritic dendritic phase. BCC (β1) dendritic phase undergoes spinodal decomposition to form a mixture of BCC_B2 (α1) and σ phases. While BCC (β2) interdendritic phase also undergoes solid-state transformation to form BCC_B2 (α2) and BCC (γ) phases.
- In the powder metallurgy route, the sample was synthesized through mechanical alloying cum spark plasma sintering technique. W-containing spark plasma sintered HEAs reveal the presence of ordered B2, BCC solid solution phase (β), FCC solid solution phase (α), and sigma phase. It is found that the number of phase formation in HEAs is less than the predicted phase formation by the equilibrium Gibbs phase rule. Around 95% relative density is observed in the spark plasma sintered W-containing HEAs, and the detailed sintering mechanism has been understood.
- The studied HEAs exhibit outstanding hardness (approx. 13.5 GPa) and modulus of elasticity (approx. 202 GPa) with tungsten, which is a signpost that the HEA is a suitable contestant for the high-temperature and wears resistance applications.
- A novel high entropy alloy AlCrFeMnNiW is synthesized using high-energy ball milling, and its structural and morphological properties are investigated. Hydrogen sorption on AlCrFeMnNiW alloy is investigated through the volumetric method, and maximum storage capacity is estimated as 0.616 wt% at room temperature and pressure with a single exposure. The activation energy of -8.161 KJ/mol has been evaluated during the desorption of hydrogen

- Heat treatment of AlCrFeMnNiWx HEAs have been performed successfully in different temperature and appropriate softening along with grain coarsening has been observed.
- The high temperature oxidation of the AlCrFeMnNiW_X (x = 0, 0.05, 0.1, 0.5 mol) HEAs presents the linear and parabolic kinetics behavior in the investigation period. The element W (up to 3.59 wt%) promotes the oxide formation at 700 °C while further addition of W limiting (up to $\Delta w = 5 \text{mg/cm}^2$) the oxide formation except for 0.05W alloy at 800°C. Furthermore, the lattice distortion may be a probable reason for the high oxidation in the tungsten added HEAs
- Successfully Applied the predictive backpropagation ANN model for different properties prediction, i. e. hardness, and mass gain at high-temperature oxidation, which enlightened the excellent agreement with experimental data.

- > The HEAs to be investigated for high-temperature Mechanical properties.
- > An extensive study could be done for hydrogen storage of the HEAs.
- > In-depth Oxide layer study and explore the various oxide present in the HEA
- > More studies on the present HEAs will provide potential application areas.

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