Phase equilibria and corrosion behaviour of Fe-Co-Ni-Mn-Cr-V-Zr high entropy alloys: An experimental and simulation study

M.Tech. Thesis

By ASHOK KUMAR



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020

Phase equilibria and corrosion behaviour of Fe-Co-Ni-Mn-Cr-V-Zr high entropy alloys: An experimental and simulation study

A THESIS

Submitted to the Graduate Faculty of

Indian Institute of Technology Indore

in Partial Fulfillment of the Requirement for the degree

of

MASTER OF TECHNOLOGY IN METALLURGY ENGINEERING AND MATERIAL SCIENCE (MEMS)

by Ashok Kumar



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Phase equilibria and corrosion behaviour of Fe-Co-Ni-Mn-Cr-V-Zr high entropy alloys: An experimental and simulation study" in the partial fulfillment of the requirements for the award of the degree of MASTER OF TECHNOLOGY and submitted in the DEPARTMENT OF METALLURGY ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2018 to June 2020 under the supervision of Dr. Sumanta Samal (Assistant Professor) and Dr. Mrigendra Dubey (Assistant Professor), Department of Metallurgy Engineering and Material Science (MEMS) Indian Institute of Technology (IIT) Indore. The matter presented in this thesis has not been submitted by me for the award degree of to another institute for any students.



Signature of the student with date (ASHOK KUMAR)

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

S. Samel

Signature of the Supervisor of M.Tech. thesis **DR. SUMANTA SAMAL**

M. Dut 29/06/2020

Signature of the Supervisor of M.Tech. thesis **DR. MRIGENDRA DUBEY**

ASHOK KUMAR has successfully given his/her M.Tech. Oral Examination held on 25 June 2020

M. Dut.

Signature of Supervisors of M.Tech. thesis Date:

Convener, DPGC Date:



Signature of PSPC Member Date:

Signature of PSPC Member Date:

ACKNOWLEDGEMENTS

I would like to thank the IIT Indore faculty and staff for their commitment to educating their students. I would especially like to thank Dr. Sumanta Samal and Dr. Mrigendra Dubey for the guidance he provided throughout this project.

And I am also thankful to the HoD MEMS and the faculty of this institution for their support and effort in teaching the concepts in Materials Science and Engineering.

I would like to take this opportunity to thank my PSPC members Dr Eshwara Prasad Korimilli and Dr. Vinod Kumar (HOD) for their valuable time in assessing my work during the mid-term and end-term presentations and giving me valuable suggestions related to my work.

Finally, I thank my parents, friends and classmates for their constant support.

DEDICATION

Dedicated To my Guide My Parents My Teachers My Classmates My Friends

Abstract

The present study reports the design and development of multicomponent $Fe_{35-v}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_v$ (y = 0, 2, 4, 6, 8, 10 at. %) high entropy alloys (HEAs) by integrated approach of combining thermodynamic simulation and experimental methods. The multicomponent HEAs are prepared by vacuum arc melting cum casting technique under the pure argon gas environment. The effect of Zr on microstructure evolution of Fe-Co-Ni-Mn-Cr-V HEAs is systematically investigated to understand the phase equilibria of designed HEAs using both thermodynamic simulation and the experimental results. The corrosion behaviour of Fe-Co-Ni-Mn-Cr-V HEA is investigated using potentiodynamic polarization method, immersed in 3.5 wt. % NaCl electrolyte medium at room temperature and compared with the corrosion behaviour of conventional SS136 stainless steel, indicating that the corrosion resistance of designed HEA (corrosion rate = 0.0763 mmpy) is comparable with the conventional SS 316 steel (corrosion rate = 0.0527 mmpy). The experimental galvanic corrosion data as well as material data of FeCoNiMnCrV HEA was utilized to perform galvanic corrosion and crevice simulation by finite element model method using Comsol multiphysics software to understand the distribution of potential and current density in the electrolyte medium.

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LIST OF SYMBOLS

i	Current density (Am ⁻²)
q	Charge density (Cm ⁻³)
t	Time (s)
n	Number of electrons transferred (unit-less)
F	Faraday's constant (96500 C/mol)
E	Electric field intensity (NC ⁻¹)
σ	Conductivity ($\Omega^{-1} m^{-1}$)
Ø	Corrosion potential (V)
Øo	Free corrosion potential (V)
i ₀	Free current density (Am ⁻²)
CR	Corrosion rate (mm year ⁻¹)
ν	Reaction rate (mol $m^{-2} s^{-1}$)
ρ	Density (kg m ⁻³)
$M_{\rm w}$	Molecular weight (kg mol ⁻¹)
a_{a}	Anodic transfer coefficient (V)
$a_{ m c}$	Cathodic transfer coefficient (V)
α	Anodic Tafel parameter (V)
β	Cathodic Tafel parameter (V)
e⁻	Electron

GLOSSARY

Anode -

The portion of a galvanic couple which sees a decrease in potential along the electrode surface

Cathode -

The portion of a galvanic couple which sees an increase in potential along the electrode surface

Electrolyte -

A solution capable of carrying/transferring charge

(Electrochemical) Potential -

The measure of the voltage in a system

Galvanic Corrosion -

"The corrosion that occurs as a result of one metal being in contact with another in a conducting environment" [27]

Overpotential -

The difference between the actual potential and the free potential

ACRONYMS

BCC	Body centered cubic
EDX	Energy dispersive X-ray spectroscopy
FCC	Face centered cubic
HEA	High-entropy alloys
SEM	Scanning electron microscope
XRD	X-ray powder diffraction
CR	Corrosion rate

Chapter 1

(a) Introduction

1.1 Overview

In this thesis, the corrosion behavior and simulation of high entropy alloys (HEAs) synthesized by the solidification route have been studied for potential applications.

1.2 High Entropy Alloys

High-entropy alloys (HEAs) are the solid solution of multicomponent alloys composed of at least five elements with compositions of 5-35 atomic % for each element [1], and therefore recently HEAs are the most attracting composition due to unique microstructure, high corrosion resistant, high temperature strength and also has been adjustable mechanical, magnetic, electrical and chemical properties. Generally, the principal element of HEA consists always more than five percent atomic fraction. HEAs was first reported by the Yeh et al., followed by the Cantor et al [1, 2].

Cantor et al. explained that the more knowledge is available about to development of alloys based on the one or two components, but there is no or limited knowledge about the development of near-equimolar concept based alloys [3].

The properties of crystalline phases and structure were restricted to alloy based on one or two main components on the occurrence of work theoretically and experimentally. Therefore, the more information is required to develop the alloys/metals very close to the corners and edges of the multicomponent in HEA phase diagram, but with the less information about center of the phase diagram, and this imbalance is important to understand the ternary alloys/HEAs. But it's much clear with the increasing number of components. Therefore, there is no information available at the center of the phase diagram except those multicomponent HEA system that is reported recently. Therefore, the study of microstructure of HEAs is very useful at ambient temperature as potential candidate which improve the properties of the alloys, and can lead to the formation of fine precipitation due to kinetics.

1.3 Core effects of high entropy alloys

The HEAs consists at least five elements with the atomic percent 5-35 %, which forms the complex system Their structure and properties normally depends on the four major core effects. Yeh suggested the four core effects that describe the properties of multicomponent HEAs [3]

1.3.1 High entropy effects

The high entropy effects play a big role to enhance the formation of solid solution phase(s) and form simple microstructure. The high entropy effect has higher tendency to the formation of disordered solid solution than the order intermetallic compound and Laves phase. Due to the high entropy effects, alloys lead to the formation of solid solution rather than the Laves phase and intermetallic compound in the HEAs [3]. Based on the one major element based alloys, ΔH_{mix} and ΔS_{mix} is found to be negative in the presence of elemental phases. But ΔH_{mix} is so much negative as compared to ΔS_{mix} in compound phase, because ordered structures have very less configurational entropy, and ΔS_{mix} have highest negative in the multicomponent which contains the random solid solution phases.

It is well known that the Gibbs free energy of mixing, ΔG_{mix} , is expressed as

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

 ΔH_{mix} and ΔS_{mix} are the enthalpy of mixing and entropy of mixing respectively. The mixing of entropy ΔS_{mix} is large at higher temperature. Therefore, ordered intermetallic phases are very less stable rather than the

disordered solid solution phase at high temperature. Hence, the mixing free energy decreases on the increasing of number of elements. It is also found that the stronger bond energies will enhance the formation of solid solution phase rather than intermetallics.

1.3.2 Sluggish diffusion effect

HEAs consist of solid solution phases along with ordered solid solution, due to sluggish diffusion of atoms, leading to chemical stability of the HEAs. The Sluggish diffusion helps in improving the properties of alloys. It also improves the creep property of HEAs at higher temperature and hence increases the life of material. It is important to understand that the slower diffusion would occur in the HEAs due to larger fluctuation of lattice potential energy between lattice sites. The sluggish diffusion leads to finer grain structure, leading to the improvement in toughness and strength of materials. It is also found that the creep property is also improved due to sluggish diffusion, causing prolong life of materials at high temperature.

1.3.3 Severe lattice distortion effect

In the HEAs, each atom is surrounded by different kinds of atoms, causing severe lattice strain and stress due to the atomic size difference, the different crystal structure and bonding energy of individual elements in HEAs. It is reported that the lattice distortion affects the various properties such as thermal property, electronic conductivity etc. It is observed that the electrical conductivity decrease in HEAs due to electronic scattering. The phonon scattering plays big role to decrease the thermal conductivity of HEAs.

1.3.4 Cocktail effects

The word "Cocktail effect" was first coined by the Prof. Ranganathan to understand the behavior of HEAs. [4]. The enhancement of properties HEAs may be due to interaction of different properties of different constituent phases present in HEAs. The variation of property in HEAs arises due to basic properties of elements and the mutual interactions among all the elements in the alloys. Generally, the mixture rule is applied to calculate the values of properties in conventional alloys system but when the same rule is applied in HEAs, there is severe difference between the calculated value due to the mixture value and experimental value. Both lattice distortion and mutual interaction play big role to change the properties of HEAs. There are some properties in the HEAs such as high strength, good plasticity, high magnetization, high electrical resistance and low coercively etc. which is explained by the cocktail effect.

1.4 (b) Literature Review

High-entropy alloys (HEAs) are typically defined as alloys containing five or more elements with the composition of each element in the alloys ranging between 5-35 at.% [6,7,8, 7]. Therefore, the HEAs show better mechanical, electrical and magnetic properties as compared to conventional alloys. The discovery of HEAs is a revolution in the field of metallurgy as it leads to the exploration of new materials and novel properties. HEA exhibits excellent physicochemical properties such as magnetic, electrical and mechanical properties [9] and it also shows better properties such as high corrosion resistance, resistance to wear, high temperature strength and oxidation, making them promising candidates for future engineering applications [10,11,12]. It is reported in the open literature that HEAs show some advantages such as softening resistance at elevated temperatures [1, 13] and sluggish diffusion kinetics [14], Therefore, HEAs are considered as a future material due to high corrosion resistance, wear resistance etc. It is observed that the single phase HEAs show some problem because of their balancing ductility and tensile

strength [6, 7]. HEAs show better ductility due to FCC crystal structure but not exhibit enough strength to protect from the fracture under service [15, 16]. Whereas BCC crystal structure based single phase HEAs show better strength [17]. Therefore, researchers are doing research work in the direction of developing composite HEAs to solve the problem of brittleness. The composite HEAs consisting of BCC and FCC solid solution phases exhibit excellent mechanical property in terms of strength and ductility [18]. There are some other difficulties such as poor castability of HEAs and improper homogeneity, which degrades the mechanical properties of HEAs and reduces the material quality, which limit the use of HEAs for engineering applications [8, 19]. Finally, the researchers solve the above problem by developing the eutectic high entropy alloys (EHEAs). EHEAs consisting of mixture of both soft FCC and hard BCC phases provide good ductility along with good strength, which helps in providing sufficient fracture strength and high ductility. [20]. There are also other advantages in the use of EHEAs [20,21] which is, low energy phase boundary, high rapture strength, Excellent high temperature creep resistance, controllable microstructure, stable defects structures [21]. It is to be noted that the above poor cast-ability problem was also solved by use of EHEAs and hence improved the mechanical properties.

Three are various techniques to develop the HEAs, which is

- 1. Arc melting technique
- 2. Thin film sputtering technique
- 3. Laser cladding technique
- 4. Furnace melting technique etc.

The most widely technique for the making of HEAs is the melting and casting route and this route is economical and feasible. The melting route is widely used for developing the HEAs by melting most of the metals having temperature of more than 3000 °C.

Chapter: 2

(a) **Processing Routes**

There are many techniques available to make the high entropy materials, but in current the research work, the solidification technique was used for preparing HEAs

2.1 Sample Preparation

Fe, Co, Ni, Mn, Cr, V and Zr (>=99.9%) were used as the primary materials in the form of solid granules to prepare HEAs cast-ingots by the arc melting technique using under the high purity argon gas environment to obtain arc melted alloy buttons and Pancake obtained from pre-melted homogeneous buttons. Approximately 500g of raw materials were used to make the buttons under the water-cooled copper hearth in the vacuum chamber. The buttons were melted five times to obtain the chemically homogeneous cast ingots and which was used to determine the corrosion rate through the experimental technique and also by the finite element simulation in COMSOL multiphysics software.

The samples were prepared for the testing before each electrochemical experiment in the NaCl solution by the hand polishing machine and SiC grinding papers were used up to grade 2000. The sample was cleaned by acetone and distilled water in the ultrasonic cleaner after complete one grade polishing. The sample was dried using the drier and screwed tightly to a rod sample holder before immersion in the NaCl electrolyte solution for performing the galvanic corrosion.



As-cast button

Pancaked sample

Fig 2.1 Homogeneous as-cast sample of multicomponent HEAs.

2.2 Solidification Route

The solidification route is widely used technique for synthesis of the HEAs. The vacuum arc melting process is popular because it attains the temperature up to 3000°c, which is used to melt most of the metals during casting of HEAs. The vacuum arc melting cum casting unit is used to develop the both equimolar and non- equimolar HEAs. The vacuum arc melting cum casing unit gives some disadvantages during the making the HEAs such as improper vaccum creation, evaporation of low temperature melting metals like aluminum, difficult to control the copper composition in the HEAs during manufacturing, inhomogeneous casting due availability of high temperature materials like Tungsten, Titanium etc. The

vacuum arc melting cum casting unit was used for the production of metal ingot. The casting unit consists three different units as fallows.

- i. Vacuum unit
- ii. Chilling unit
- iii. Welding unit

2.2.1 Vacuum Unit

The vacuum unit is used to make the alloys in the vacuum chamber and all the switches used are based on pneumatic control Turbo pump are direct coupled with the vacuum unit that's used to generate the vacuum in the vacuum chamber which is marked in Fig. 2.2 The tungsten electrode is used to melt the alloys in the chamber in water-cooled copper mold. During the melting of alloys, the direct current (DC) is used to generate the arc between metal and electrode in the presence of argon environment.



Fig 2.2 Image of vacuum arc melting cum casting machine

2.2.2 Welding unit

In the welding unit, TIG welding is used for melting the alloys by constant DC power supply source. The different size electrodes are used for casting of alloys, therefore maximum current is reached around 300 A during the melting of buttons in the vacuum chamber, and reached 400A when used another size of tungsten electrode to make the big sample such as pancake. The max. DC voltage is used around 30000mV for the supply of current to maintain the proper arc between electrode and metals.

2.3.3 Chilling unit

The chilling unit is also coupled with the vacuum unit and used for decreasing the temperature of both copper mold and tungsten electrode. The distilled water is used for fast cooling of electrode and die.

(b) Methodology

2.3 X ray Diffraction (XRD)

The XRD is standard technique, that's generally used for the phase evaluation of material. In the XRD, incident rays directly fall on the polished sample, and produced constructive interference, when conditions satisfy the Braggs law ($n\lambda$ =2d sin θ). The XRD measures average spacing between layers and row of atoms, and provide the exact information of crystal structure of materials. The Braggs law relates with the wavelength of electromagnetic radiation for lattice spacing and diffraction angle for the crystalline sample. It also helps in measuring the shape and size by diffracting X-rays from the crystalline sample. The structural characterization of HEA was carried out by using (X-pert pro instrument) with the Cu-K_{α} (λ = 0.154056 nm) radiation. The XRD was operated at 30

mA and 45 kV with the step size $2\theta = 0.017$ degree, and peak was identified by using International Committee for Diffraction Data (ICDD).

2.3.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope is used for the purpose of surface analysis of the materials which works at very small wavelengths around (3.7 pm at 100 keV). The surface morphology of the materials is examined by the deflection of electrons. The electron interacts with the surface of materials such as backscattered electrons, X-rays and secondary electrons, and magnetic field plays big role to deflect electrons from the surface. The backscattered electrons having higher energy than the secondary electron therefore backscattered electrons reflect from the sample surface after interacting the material surface via elastic scattering, whereas secondary electrons reflect from the material surface via inelastic scattering. The morphology and topology of the materials can be studied up to resolution 10 nm in the scanning electron microscope, which shows all the phases clearly such as grain boundary, precipitates, inclusions, pores and voids. Therefore, SEM is very useful for phase contrast analysis due to the atomic number (Z) contrast of different elements and also an essential tool for texture analysis of metals/alloys.

2.3.2 Energy Dispersive Spectroscopy (EDS)

The INSPECT F SEM coupled with Oxford INCA 300 X-ray energy dispersive Spectroscopy (EDS) was used to identify the elemental composition of a metals/ alloys.

Chapter 3

3.1 (a) Thermodynamic parameters

It is important to note here that three basic thermodynamic parameters such as ΔH_{mix} , ΔS_{mix} , and ΔG_{mix} are generally used to predict phase stability in the HEAs. The first study on phase stability in HEAs was reported by Zhang et al [1] Therefore, the main focus is to understand the behavior of individual elements and its interaction with the other alloying elements. The statistical method was used to analyze the collective behavior of elements by using a large database of HEAs to control phase stability and to understand the formation of different phases in the HEAs such as intermetallic solid solution and Laves phase. There are some other factors such as Hume-Rothery parameters and thermodynamic parameters that are described below briefly.

i. Enthalpy of Mixing (ΔH_{mix})

The enthalpy of mixing is defined as the summation of both internal energy and flow energy in the system. The enthalpy is a thermodynamic parameter, which is described as follows

$$H = U + PV$$

The flow energy is described by the product of pressure and volume in the system, and the expression of enthalpy of mixing for the HEA was taken from reference [22].

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} c_i c_j; \left(\Omega_{ij} = 4 \Delta H_{ij}^{mix} \right)$$

Where ΔH_{ii}^{mix} = enthalpy of mixing for binary liquid metals/alloys ij, and

 C_i = Concentration of ith element

 $Cj = concentration of j^{th}$ element

ii. The entropy of mixing or configuration entropy (ΔS_{mix})

The entropy of mixing is also called the configuration entropy that is the extensive thermodynamic quantity when two different elements are mixed together. The entropy of mixing is increased by the addition of different elements at different temperatures and pressures. The configurational entropy refers to the distinguishable ways of arranging the atoms in the system on the lattice site, and the configuration entropy is expressed as.

$$\Delta S_{mix} = -R \sum_{i=1}^{n} (c_i \ln c_i) \dots [22]$$

The value of ΔS_{mix} is always between 12 to 17.5 J/K mol for the HEAs, as listed in Table 5.6.

iii. Gibbs free energy (ΔG_{mix})

The Gibbs free energy is calculated by using two different thermodynamic parameters i.e. mixing of enthalpy and mixing of entropy. The Gibbs free energy is generally used to predict the process of the system at a given temperature and pressure.

According to Gibbs free energy relation, it shows the spontaneous behavior of the process for negative values of ΔG_{mix} and shows nonspontaneous behavior at the positive values.

 $\Delta G_{mix} = \Delta H_{mix} - T_m \Delta S_{mix} \dots [22]$

Where, ΔH_{mix} = mixing of Enthalpy for an alloy.

 Δ Smix = mixing Entropy for alloy

 T_m = Temperature of combined elements.

iv. Thermodynamic Parameters (Ω)

The new parameter Ω was used to understand the combined effect of both entropy of mixing and enthalpy of mixing for phase formation in the HEA [22]. The values of ΔS_{mix} and ΔH_{mix} was compared to judge the formation of phases in the developed alloy. As we know that both entropy of mixing (ΔS_{mix}) and enthalpy of mixing (ΔH_{mix}) play a different role in the formation of solid solution phase.

According to the relationship, the term $(T_m) \Delta S_{mix}$ gives the higher value at high temperature i.e. compared with the magnitude of (ΔH_{mix}) . The values of enthalpy of mixing is in KJ/mol, which is listed in Table 5.6. We observed that Ω parameter values are continuously decreasing with the increasing zirconium content in the HEA.

Therefore, $(T_m) \Delta S_{mix}$ is the main factor that plays a big role to affect the formation of a solid solution in the alloy.

$$\Omega = \frac{(T_m) \,\Delta S_{mix}}{\Delta H_{mix}}$$

Where Ω is a derived thermodynamic parameter

1. If the $\Omega > 1$, shows the formation of solid solution phase in the HEA, because of more contribution of $(T_m) \Delta S_{mix}$ than that of the (ΔH_{mix}) .

2. If the $\Omega = 1$, it is used as a critical value to understand the behavior of the formation of solid solution phase.

3. If the $\Omega \leq 1$, it shows the formation of intermetallics and segregations. Therefore, Ω values are used to estimate the formation of a solid solution. The melting temperature (T_m) of HEAs was calculated using Vegard's mixture rule,

$$T_m = \sum_{n=1}^n (c_i (T_m)_i)$$

v. Atomic size difference (δ)

The parameter (δ) is generally used to know the effect of the size of constituent elements in HEA, and it gives the proper information about formation of phases [22].

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\overline{r}}\right)^2}; \overline{r} = \sum_{i=1}^{n} c_i r_i$$

; where r_i is the radius of the ith element and \bar{r} is the mean radius of alloy.

 $C_i = concentration of each element$

vi. Valence electron concentration (VEC)

The valence electron concentration (VEC) relation is generally used to determine the formation of solid solution phases in the developed HEA [23]. The mixture rule technique was used to calculate the values of VEC by using the concentration of i^{th} element and valence electron concentration of ith element.

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

; where $(\text{VEC})_i$ is the valence electron concentration of the i^{th} element in the HEA.

The values of VEC signifies the possible phase formation in the HEA with the addition of zirconium.

If the value of VEC

(i) \geq 7.95 (FCC solid solution phase only)

- (ii) $7.71 \le VEC < 7.86$ (FCC, BCC and Laves phase co-exists)
- (iii) < 7.63 (FCC, Laves and intermetallic phase co-exists)

vii. Electronegativity ($\Delta \chi$)

The electronegativity difference is considered as Hume-Rothery parameter that is generally used to determine the formation of intermetallic in the complex alloy system, and also help to understand the electronegativity difference behavior between the constituting elements [23]. It also plays an important role in developing the intermetallic in the HEAs.

$$\Delta \chi = \sqrt{\sum_{i=1}^{n} c_i \left(\chi_i - \overline{\chi}\right)^2}; \overline{\chi} = \sum_{i=1}^{n} c_i \chi_i$$

Where, $\bar{\chi}$ is the mean Pauling electronegativity for the HEA, and χ_i is the Pauling electronegativity for the ith element, C_i is the concentration of ith element.

viii. Λ – Parameter

The Hume-Rothery parameter Λ are generally used to understand the combined behavior of entropy of mixing (ΔS_{mix}) and atomic size difference (δ) on the formation of solid solution phases in the HEAs. Therefore, parameter Λ is also used to understand the formation of compound and its volume fraction [24].

$$\Lambda = \frac{\Delta Smix}{\delta^2}$$

If the value of Λ – Parameter is greater than equal 2.3403, it leads to the formation of single solid solution phase, and if the value lies between the

ranges 0.3165 to 0.5425, it shows the formation of solid solution phase and Laves phase. If Λ – Parameter has values less than equal to 0.2567, it shows the formation of solid solution phase, Laves phase, and intermetallics.

3.2 (b) Thermodynamic simulations

The thermodynamic simulation was done to predict the phases formation in multicomponent HEAs. The CALPHAD approach was used to predict the phases in the developed multicomponent HEA. It is to be noted that some thermodynamic functions such as Gibbs free energy (G), Helmholtz energy (A) were used to evaluate different phases under the CALPHAD approach [25].

The thermodynamic simulation was carried out using ThermoCalc[®] software with the TCHEA2[®] database for phase prediction in HEAs. The thermodynamic simulation of multicomponent Fe_{35-y}Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr_y (y=0, 2, 4, 6, 8, 10) HEAs was carried out to predict the phase formation.

Fig. 3.1 (a1) and (b1) show the plot between the mole fraction Vs. temperature and temperature Vs. Amount of phases for HEA with zirconium (Zr = 0 %) which reveals the formation of FCC_L12 solid solution phase during solidification of liquid. The mole fraction Vs. temperature plots shows the formation of around 90 % of FCC_L12 phase, indicating the existence of large solubility range. It is observed that 90 % of liquid gets solidify to form FCC_L12 phase on the decreasing temperature below 1310 °C, according to the following phase reaction.

 $(L=L+FCC_L12)$

The remaining liquid (L_1) solidify to form another phase and the remaining liquid is converted into FCC_L12 solid solution phase and ordered BCC_B2 through the following solidification reaction.



 $L_1 = BCC_B2 + FCC_L12$

Fig. 3.1 Phase diagram a1) Phase fraction *Vs*. Temperature Phase diagram b1) Solidification diagram of Fe₃₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₀ HEA.
While the thermodynamic simulation results of HEA with Zr= 2 % shows the formation of different phases during the solidification i.e. FCC_L12 solid solution phase and different intermetallics (SIGMA, C15_LAVES and Ni₇Zr₂).

Fig. 3.2 (a2) shows the mole fraction of solid *Vs.* temperature, indicating 70 % of the liquid solidify into FCC_L12 on the decreasing temperature according to the phase equilibrium reaction: $L = L_1 + FCC_12$, followed by different phase equilibria reactions involving three phase mixture (L+FCC_L12+SIGMA), three phase mixture(L+C15_LAVES+FCC_L12) and four phase mixture (L+C15_LAVES+FCC_L12+Ni₇Zr₂). Fig. 3.2 (b2) shows the plot between temperature *Vs.* amount of phase, revealing formation of different ordered and disordered phases at various temperatures.





Fig. 3.2 Phase diagram a2) Phase fraction Vs Temperature Phase diagram
b2) Solidification diagram of Fe₃₃Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₂ HEA

The Thermo-calc simulation for Fe₃₁Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₄ HEA is shown in Fig. 3.3 (a3). Firstly, the liquid solidifies into FCC_L12 solid solution phase at temperature 1280 °C, and the diagram (b3) shows the of plot between temperature Vs. fraction solid of of Fe₃₁Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₄ HEA, indicating formation various phases during phase transformation at different temperature. The different phase equilibria reaction during liquid to solid transformation is given by following reactions involving liquid and different solid phases such as two mixture $(L+FCC_L12),$ three phase phase mixture (L+FCC_L12+SIGMA), three phase mixture(L+C15_LAVES+FCC_L12) and four phase mixture (L+C15_LAVES+FCC_L12+Ni₇Zr₂).



Fig. 3.3 Phase diagram a3) Phase fraction Vs Temperature Phase diagram b3) Solidification diagram of $Fe_{31}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_4$ HEA

The Thermodynamic simulation multicomponent of Fe₂₉Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₆HEA is shown in Fig. 3.4. It is observed that the SIGMA is evolved from the liquid. The different phase equilibria reaction involving various phases is given by two phase mixture (L+SIGMA), three phase mixture (L+FCC_L12+SIGMA), three phase mixture(L+C15_LAVES+FCC_L12), four phase mixture and five (L+C15_LAVES+FCC_L12+Ni₇Zr₂) phase mixture $(L+C15_LAVES+FCC_L12+Zr_8Ni_{21}+Ni_7Zr_2)$. Fig.3.4 (b4) is the plot between temperature Vs. amount of Phase, revealing the formation of ordered and disordered phases at different temperatures.





Fig. 3.4 Phase diagram a4) Phase fraction Vs Temperature Phase diagram b4) Solidification diagram of Fe₂₉Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₆ HEA

The simulation result of Fe₂₇Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₈ HEA is shown in Fig. 3.5 (a5), revealing liquid gets converted into solid phases by various way of solidification. The solidification pathways are given by taking various phases involving two phase mixture (L+SIGMA), three phase mixture $(L+FCC_L12+SIGMA),$ four phase mixture (L+BCC_B2+FCC_L12+SIGMA), five phase mixture (L+BCC_B2+C15_LAVES+FCC_L12+SIGMA), four phase mixture $(L+C15_LAVES+FCC_L12+Ni_7Zr_2)$ and five phase mixture (L+C15_LAVES+FCC_L12+ Zr₈Ni₂₁ +Ni₇Zr₂). The diagram (b5) shows fraction Vs. plot of multicomponent phase temperature Fe₂₇Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₈ HEA, revealing formation different phases during phase transformation.



Fig. 3.5 Phase diagram a5) Phase fraction Vs Temperature Phase diagram b5) Solidification diagram of $Fe_{27}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_8$ HEA

The thermodynamic simulation result multicomponent of Fe₂₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₁₀ HEA is shown in Fig. 3.6. The solidification route is shown in Fig.3.6 (a6). The phase equilibria reactions involving different phases are two phase mixture (L+SIGMA), three phase mixture (L+C15_LAVES+SIGMA), four phase mixture $(L+BCC_B2+$ C15_LAVES+SIGMA), four phase mixture $(L+BCC_B2+$ three C15_LAVES+FCC_L12), phase mixture (L+C15_LAVES+FCC_L12), four phase mixture $(L+C15_LAVES+FCC_L12+Ni_7Zr_2)$ and five phase mixture $(L+C15_LAVES+FCC_L12+$ Zr₈Ni₂₁ +Ni₇Zr₂). Fig. (b6) shows the amount of phase Vs. temperature plot of Fe₂₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₁₀, revealing formation different phases during liquid to solid as well as solid to solid phase transformation at various temperatures.





Fig. 3.6 Phase diagram a6) Phase fraction Vs Temperature Phase diagram b6) Solidification diagram of Fe₂₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₁₀ HEA

Chapter: 4

4 (a) Corrosion Simulation

Corrosion is the deterioration of materials by the chemical/electrochemical reaction to its environment. The world is facing materials loss related problems and losing trillions economy in the prevention of corrosion. While the cost of corrosion in the global is reached 2.5 trillion dollars per year, which is 3.4% of the world's gross domestic product (GDP) [26]. Moreover, corrosion destroys every year around more than three percent of the world's GDP. Therefore, the famous institutes and universities and strong economic countries are spending lots of budget for the development of high corrosion-resistant structural or functional materials and investigating of corrosion behavior of materials to make the enormous economic benefit. There are some metallic materials and noble metals, showing higher corrosion resistance such as Gold (Au), Silver (Ag), and Platinum (Pt), etc. and poor mechanical properties [27]. Therefore, these expensive materials are limited for general applications. Hence, Famous institutes and universities are mainly focusing to develop the least expensive category materials/alloys such as stainless steel series, titanium alloy, nickel-based alloy, and so forth. A mostly conventional technique used for developing the alloys/ metals is by the addition of alloying elements in relatively low concentration to one base metal, which improves the corrosion-resistant of metals/alloys. Where the elements such as Chromium (Cr), Molybdenum (Mo), Nickel (Ni) are widely used as an alloying element in the one base metal for the formation of new alloy/metals, that provides protective passive film on the surface of the alloy/metals and also prevents from the corrosion of metals/alloys[28,29]. The alloy/metals have impurities such as precipitates, nitrides, carbides, and intermetallic compounds, which impact the corrosion behavior Therefore, industries, use higher corrosion-resistant ability material or alloys. Moreover, in the conventional alloys, both mechanical properties

and corrosion-resistant materials deteriorate at high temperature due to insufficiently high-temperature stability [30], and hence restrict their application in the highly sensitive engineering service environments. The philosophy of multicomponent high entropy alloys (HEAs) is obtained from the use of multiple elements in equimolar or near equimolar ratio. HEA is defined as the alloy that contains at least five or more than the five principal elements. The designed HEA can be equimolar and nearequimolar ratio. The atomic percent of each element varies from 5-35 at. % [31-35]. Because of the high mixing entropy effect, HEAs tend to form different types of disordered solid solutions with body-centered cubic (BCC), face-centered cubic (FCC) [33, 36], or hexagonal closed pack (HCP) [33,36-39] structures, instead of complex intermetallic compounds. The corrosion behavior of the HEAs has already been investigated earlier in the aqueous medium or environments (acid, saltwater, high temperature, and high-pressure water) [41-46]. The HEAs contain some passive elements, such as Cr, Mo, Ni, etc. Therefore, HEAs show superior corrosion resistance due to combined effect of multiple passive elements [41,42] and also have better mechanical properties such as high fracture toughness [52,53], high thermal stability [54], improved fatigue resistance [49-51], and high strength with the ductility [47,48] as compared to conventional alloys. The HEAs are highly demanded potential material for the extreme service in industries such as aerospace industries, turbine, nuclear, because of superior properties. The HEA is also used as a thin film coating on the different alloys for improving corrosion resistance property because of high cost of bulk HEAs and hence the surface coatings of HEAs on the stainless steels, Al- alloys and Si were successfully carried out via laser cladding technique [55-58], magnetron sputtering [60-62], electro spark deposition [59], etc. The coating of HEAs forms a thin layer on the alloys/metals that act as a barrier between base metals/alloys and environments and protect the coated metals/alloys from the interaction of electrochemical reaction. The novel corrosion resistance

and combination of mechanical properties of HEAs provide outstanding cavitation erosion-resistant property in the saltwater [63]. The multicomponents HEAs coating are used in the high and low-pressure vessel example (airplane, submarine, ships, and nuclear fuel tanks) to protect from the corrosion [64]. Moreover, it is important to understand that a HEA film that has the same composition of HEAs possesses even better corrosion resistant properties [63] due to homogeneous microstructure.

4.1 (b) Problem description

The aim of this project is to develop a high corrosion resistant HEA by the galvanic corrosion characterization using NaCl electrolyte in comparison with the conventional 316 stainless steel. The experiment data of HEA was used as input parameters to carry out finite element method corrosion simulation of HEAs by Comsol multiphysics software. There are some factors that can contribute to the amount of corrosion of alloy/metal such as types of electrolyte, environments, ingot casting, chemical homogeneity and purity of elements [65]. The galvanic couple geometries are evaluated after development and validation of the designed HEA using finite element method. Therefore, in this project a simple model of coplanar electrodes is utilized (as shown in Fig 1) and that can be allowed the initial focus to be on development of the boundary conditions rather than generation of geometry representing a specific system. The galvanic couples of one cathode and one anode are used. Both corrosion rates and current densities of HEA along with the anode surface are generated to quantify to amount of corrosion [66]. It is worthy to mention that the distribution of electrochemical potential describes the behaviour of the system in the presence of NaCl electrolyte.

4.2 (c) Galvanic corrosion

Galvanic corrosion occurs when two dissimilar metals/alloys make the external electrical connection within the conductive environment such as sulfuric acid, hydrochloric acid, and saltwater, etc. The environments of electrolytes provide a medium for ionic flow from anode to cathode because of metals/alloys break-down in the presence of conductive medium by the electrochemical reactions. The lower corrosion potential (Ecorr) in the galvanic couple becomes more active and corrode preferentially. The anode releases (electron and cation) in the electrolyte medium by the anodic reaction and cathode consume (electron and anion) that is released by the anodic reaction to complete the cathodic reaction, where anode and cathode are the parts of the galvanic couple when undergoes metals/alloys dissolution. The corrosion severity of the materials depends upon the various factor such as corrosion current density (I_{corr}), corrosion potential difference (E_{corr}), polarization behavior of metals/alloys, electrolyte conductivity, the distance between the dissimilar metals/alloys and the ratio of the area between anode to cathode, etc. [65].

4.3 Electrochemical experiment technique

The corrosion experiment of samples was carried out in an electrochemical workstation with the help of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). The sample fixed in the electrochemical workstation act as a working electrode, while the counter electrode, and a reference electrode was used fully platinum meshed and standard calomel electrode (SCE) respectively. The experiment was run to obtain the equilibrium potential and the electrochemical impedance spectroscopy (EIS) testing was done to obtain the resistance offered by the NaCl (electrolyte) solution between the

reference electrode (RE) and the working electrode (WE) or sample after attaining the equilibrium potential. Prior to each electrochemical experiment, samples were kept at a potential of 800 mV more negative than the potential measured immediately after immersion for 1 minute, and the open circuit potential (E_{oc}) was measured for 15 minutes. The accomplished feedback compensation technique was used to incorporate the improve electrolyte resistance in the IR connection.

The potentiodynamic polarization curves provide relationships between electric potential and current density. During the potentiodynamic polarization experiment, external potential was applied to the test samples. The potential range of SS316 was varied from 0 mV to -500 mV and -250 mV to -750 mV for HEA against the equilibrium potential with respect to standard calomel electrode (SCE). The external potential was applied at a scan rate of 1 mV/s. The applied potential was increased by multiplying the electrolyte resistance measured using EIS with the cell current. The current density result was recorded for HEA and conventional stainless steel SS316 by the changing the electric potential.

The anodic electrochemical behavior of HEA and stainless steel were determined by using potentiodynamic polarization measurements with fixed voltage scan rate of 1 mV/s applied from an initial potential of -0.25 vs. open-circuit voltage (E_{oc}) to the final potential of 1.6 V vs. open-circuit voltage (E_{oc}).



Fig. 4.1 Image of electrochemical work-station

4.4 Corrosion rate calculation

The electrochemical corrosion test was performed on the HEA and stainless steel (SS316) sample of size 20 mm \times 30 mm by the potentiodynamic polarization measurement using aerated 3.5 wt.% NaCl (electrolyte) solution in the distilled water at the room temperature. The electrochemical corrosion result was recorded at a scan rate (1 mV/s) by using the CHI604E type electrochemical workstation. During the electrochemical test, the sample was established at the initial and final potential in the range of (-0.5 to 0 V) for HEA, similarly, SS316 was also placed at the range (-75 to -0.25 V), where open circuit potential was obtained (-0.5277 and -0.3234 V) for HEA and SS316. Both samples (HEA and SS316) were dipped in NaCl (electrolyte) solution for 5 days

before performing the experiment test and allowing the system to reach the equilibrium with the electrolyte exposing the sample to an area of around 0.78 cm² to the solution. The corrosion rate was calculated for each metal/alloys by using the following relation.

Corrosion rate (mm/year or mmpy) = $3.27 \times 10^{-3} \times (i_{corr} \times EW)/rho$

Where: i_{corr} = Corrosion current density in (μ Acm⁻²)

 ρ = mass density (g cm⁻³)

EW= Equivalent weight of the electrode (g)

The equivalent weight was calculated of the HEA and SS316 by using following expression.

$$EW = \left(\sum \frac{n_i f_i}{w_i}\right)^{-1}$$

;where $n_i = V$ alence electron of the ith element of the alloy

 f_i = Mass fraction of the ith element in the alloy

 $W_i = Atomic$ weight of the i^{th} element in the alloy.

4.5 Methodology of Galvanic corrosion simulation

The potential distribution in the electrolyte (sea water) of a galvanic system is fundamentally based on the continuity equation for the conservation of charge in the sea water [67].

 $-\nabla . \, i = \frac{\partial q}{\partial t}....(1A)$

For the steady state system

 $\frac{\partial q}{\partial t} = 0 \text{ and } \nabla . i = 0.....$ (2A)

The relationship between the electric potential (\emptyset) and the electric field intensity (E) is

 $E = -\nabla \phi.....(3A)$

According to Ohm's Law, we have

 $\nabla^2 \phi = 0......(6A)$

4.5.1Geometry and boundary condition

The model geometry was analyzed by using the appropriate boundary conditions. Here we have considered three different types boundary conditions at the electrode surface: Butler-Volmer, linear and exponential (Tafel).

In this project, we have utilized the finite element method using Comsol Multiphysics software to solve the Laplace equation [6A] in selected system. The simple 2D geometry was created in the Comsol software using 2D Cartesian coordinates, (as shown in Fig. 4.2).



Fig. 4.8 Image of 2D Cartesian geometry

The main assumption was considered for this system is that there is no current flow normal to the insulating boundaries [3]. According to equation [1A], charge within the system cannot change in the steady state condition, and applied zero flux at boundary 1, 2 and 3.

The Edges (A) is the electrode surface of alloys/ metals and Edges (B) consider the electrolyte boundary (artificial cathode). Here we have applied initially zero electrolyte potential at boundary (B) and Edges (A) consider as an anode surface. The Butler-Volmer equation was used to solve the kinetic process in the system.

The given Butler-Volmer relationships of current density were used based on the cahodic and anodic reactions which take place on the each electrode surface in any atmosphere. The alloys/ metals undergo the cathodic as well as anodic reaction when it acts as the cathode or anode in a galvanic couple. If anodic and cathodic currents are equal at zero equilibrium potential (overpotential), then this point is called as exchange current density, and if equilibrium potential (overpotential) is not equal to zero, both anodic and cathodic current density will be different.

The anodic current density for a given electrode is

 $i_{anodic} = i_0 \exp \left[a_{anodic} \frac{nF(\phi - \phi_0)}{RT} \right]$(7A) And cathodic current density for a given electrode

$$i_{cathodic} = -i_0 \exp\left[-a_{cathodic} \frac{nF(\emptyset - \emptyset_0)}{RT}\right]....(8A)$$

The total current density is

$$i_{Total} = i_{anodic} + i_{cathodic}$$

 $i_{Total} = i_0 \exp \left[a_{anodic} \frac{nF[\emptyset - \emptyset_0]}{RT} - i_0 \exp \left[-a_{cathodic} \frac{nF[\emptyset - \emptyset_0]}{RT} \right] \right]$ (9A)

The equation 3 is known as Butler-Volmer expression

Hence the Total current density for electrode A which acts as a cathode in geometry.

$$i_{A} = i_{0,(A)} \exp \left[a_{anodic,(A)} \frac{nF[\emptyset - \emptyset_{0,(A)}]}{RT} - i_{0} \exp \left[-a_{cathodic,(A)} \frac{nF[\emptyset - \emptyset_{0,(A)}]}{RT} \dots \right]$$
(1B)

The total current density for electrode B, which acts as a anode in geometry.

$$i_{B} = i_{0,(B)} \exp \left[a_{anodic,(B)} \frac{nF[\phi - \phi_{0,(B)}]}{RT} - i_{0} \exp \left[-a_{cathodic,(B)} \frac{nF[\phi - \phi_{0,(B)}]}{RT} (2B) \right]$$

The Butler-Volmer equation reduces to the following linear relationships for the current density-potential at given low overpotential, which is $[\emptyset - \emptyset_0] < 0.01V$

The current density-potential for Cathodic

$$i_A = i_{0,(A)} \left[\frac{nF(\phi - \phi_{0,(A)})}{RT} \right]$$
.....(3B)

And current density-potential for Anodic

$$i_B = i_{0,(B)} \left[\frac{nF(\phi - \phi_{0,(B)})}{RT} \right] \dots (4B)$$

On the other hand, Butler-Volmer equation reduces to the following linear relationships for the current density-potential at a given higher overpotential, which is $[\emptyset - \emptyset_0] > 0.01V$

$$i_{Total} = i_0 \exp\left[a_{anodic} \frac{nF[\phi - \phi_0]}{RT}\right]$$
(5B)

The expression for the overpotential is known as the anodic (Tafel) equation.

$$[\emptyset - \emptyset_0] = \alpha \log_e \left(\frac{i_{Total}}{i_0}\right).$$
 (6B)

The Butler-Volmer equation reduce for the cathodic polarization at $[\emptyset - \emptyset_0] < -0.01V$ $i_{Total} = -i_0 \exp\left[-a_{cathodic} \frac{nF[\emptyset - \emptyset_0]}{RT}.....(7B)\right]$

The overpotential expression is known as the anodic (Tafel) equation. $[\phi - \phi_0] = \beta \log_e \left(-\frac{i_{Total}}{i_0} \right).....(8B)$

$$a_{cathodic} = -\frac{RT}{nF\beta}....(2C)$$

4.6 (d) Methodology of Crevice simulation

Intense localized corrosion frequently occurs within crevice and other shielded areas on metal surface expose to corrosive environment. The crevice corrosion occurs due to narrow space between metal to metal and metal to non-metal contact areas, and also possible cause of deposition of dirt, mud, cracked part and bio fouling deposited like iron hydroxide [68].

4.6.1 Model formulation

Fig. 4.3 shows the crevice geometry that was created in two parts for the validation of model. The crevice part was developed between the HEA and Plexiglass (insulator) [68]. One is interior electrolyte domain, labeled by **region-a**, is oriented with the origin at the crevice mouth which is in the positive x-direction from the crevice mouth inward toward the crevice tip, and second is exterior domain, bulk of the electrolyte solution that is labeled by **region-b**. The width of the bulk electrolyte solution marked as (L) and the boldly exposed interior surface marked as (m). The z-direction is positive upward from the top of the crevice. The boldly exposed surface consider as an artificial electrode. It is assumed that the electrolyte in both region-a, and region-b is well mixed, and only the potential in the system is determined.



Fig. 4.3 model of the crevice corrosion.

Fig. 4.4 shows the model of crevice corrosion that was developed in the Comsol multiphysics software; baseline parameters are listed in Table 4.1 which was used to construct the geometry. The Arbitrary Langrangian Eulerian (ALE) method was used to incorporate the moving interface during corrosion, whereas ALE incorporates two frames, one is the

reference frame and second is the spatial frame. The reference frame X, Z coordinates was compared with the spatial frame X, Z coordinates for a 2-D formulation. The co-ordinates of reference frame were fixed with the time while spatial frame co-ordinates were moving with the time, on the application of boundary condition [68-70]. Therefore, moving mesh technique in the geometry was considered, and mesh displacement was obtained by solving following equations. The value of E_B and E_A was applied at the crevice mouth and boldly exposed surface that is described in equation (5). The Laplace equation (2) was solved combined region-a and region-b for the 2D numerical simulation in created geometry, and subjected boundary conditions (3), (4), (5). The equation (7) applied at the boldly exposed surface, and damage evaluation was determined by using equation (8). Pickering extended our knowledge about of crevice corrosion, the potential drop as a function of depth within the crevice, and couple potential as the driving force in the crevice system, it is observed that the anodic current flows from inside the crevice through the NaCl electrolyte towards the boldly exposed surface, and the ohmic drop down at the length of the crevice occurs. The measured magnitude of potential drop at this location of active to passive is given by the ohms law (V =IR), where the IR model derives from the critical potential drop between the boldly exposed surface (crevice mouth) and the location of critical current density (i_{crit})[68].

Where I is equal to the critical current (I_{crit}) and

- ρ = solution resistivity inside the crevice
- x = Crevice depth

A = cross sectional area which is formed by the crevice opening (gap \times width)

R is obtained by the given relationship

$$R_{\Omega} = \frac{\rho X}{A}.$$
 (1)

The model cell is a laboratory cell which consists 2 mm square outside the mouth of crevice, and used this as a bulk electrolyte domain to model the electrolyte charge transport with constant electrolyte conductivity (10 S/m). The 1 mm wide was created between the Plexiglas and a sample of HEA.

The secondary current distribution physics was used for this cell instead of primary current distribution, and was neglected mass transport effect of dissolved element of HEA and ions. The experimental polarization curve was used as electrode reaction kinetics, and set the potential of the electrode 0.5 V. where the electrolyte potential was applied 0 V at the leftmost boundary, and was used default insulation condition for all other boundaries. The electrode surface boundary node was added to model in the HEA surface deformation. The model was solved by the default non-deforming boundary on the moving boundaries for the deformed geometry. All these boundaries were straight line to improve the shape of the deformation in the corner of geometry, and change the boundary condition setting of the feature to zero normal displacement. The whole model was solved by time dependent with initialization study, which is prescribed for the 50 hours duration.

Table 4.1

Variable	Value	Units
М	15	Mm
W	1	Mm
L	4	Mm
Ν	0.82	Mm
Т	1	Mm



Fig. 4.4 Finite element model of crevice corrosion.

The Laplace equation	was used for	the potential	development in	model.
$\nabla^2 E = 0 \dots$				(2)

4.6.2 Boundary condition in region-a

The given boundary conditions are applied in region-a to evaluate the crevice result. The Plexiglas worked as an insulator in the crevice geometry.

 $\frac{\partial E}{\partial x} = 0 \text{ at } x = m......(3a)$ $\frac{\partial E}{\partial z} = 0 \text{ at } z = w.....(3b)$

The boundary condition was applied on the metal interface z = H(x, t) is due to dissolution of the HEA elements, and Ohm's Law was used to determine the damage profile.

 $k\nabla E.\,\hat{n} = -i(E).....(4)$

, where k = conductivity

 \hat{n} = unit outward normal vector to the HEA surface

i(E) = current density that is obtained from the polarization curve

The potential at the mouth of the crevice was prescribed for the one

dimensional results.

 $E = E_B \text{ at } x = 0.$ (5)

, whereas E_B is the unknown boundary that is applied potential on the mouth of crevice in region-a, and this is also similar end of the crevice mouth in region-b.



Fig. 4.5 Image of interior domain of crevice model

4.6.3 Boundary condition in region-b

Fig. 4.6 shows the boundary conditions that are applied in the bulk electrolyte, region-b, and assumed that both L and N are sufficiently large. Therefore, the following insulating boundary conditions hold in the far field.

$$\frac{\partial E}{\partial x} = 0 \text{ at } x = -L.....(6a)$$

$$\frac{\partial E}{\partial z} = 0 \text{ at } z = -N, z = w....(6b)$$

The piecewise constant function was defined for the electrolyte region $0 \le z \le w$, and boldly exposed surface of HEA $-N \le z < 0$. These function was determined along the boundary conditions x = 0.

$$E(0,z) = \begin{cases} E_B, for \ z \ge 0\\ E_A, for \ z < 0 \end{cases}$$
(7)

, where E_B is the applied unknown potential at the crevice mouth, and E_A = Potential applied to the boldly exposed surface (artificial electrode).



Fig. 4.6 Image of exterior domain of crevice model

For the 2-D numerical simulations, Laplace equation (2) is solved in the combined regions (a) and (b) subjectd to the boundary conditions (4), (5), (7) and the boldly exposed portion of (8).

This is a free-boundary problem for the damaged surface, H(x,t), whose shape is obtained from the solution of (3). An outline for the numerical computations is presented in the section on numerical solution procedures

$$\frac{\partial H}{\partial t} = \sqrt{\left(1 + \left(\frac{\partial H}{\partial x}\right)^2\right)} \quad \frac{i(E) M_{alloy}}{2F\rho_{alloy}}....(8)$$

4.6.4 Electrochemical reactions

The HEA elements convert into ions and release the electrons when it comes in contact with NaCl electrolyte, and at the same time oxygen comes in the contact of HEA surface and consume electron, leads the formation of OH^- through the cathodic reaction. The initially dissolve oxygen remains same in the electrolyte solution, shown in Fig. 4.7.

In the second stage, Fe^{++} reacts with the water (H₂O), and formed iron hydroxide at the artificial electrode surface. At the same time Cl⁻ react

with Fe⁺⁺ and form a metal chloride in electrolyte and this metal chloride also reacts with H₂O, releases H⁺, where H⁺ describe the pH value in the system. The concentration of dissolve, PH and conductivity would be same on HEA surface, and as well as bulk of the solution. The PH value decreases with increase amount of $2H^+$ ion continuously inside the crevice. Similarly, all the element of HEA will react with the dissolve oxygen which is Co, Ni, Cr, Mn and V.

First stage

 $Fe \rightarrow Fe^{++} + 2e^{-}$ anode

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ cathode

Second stage

 $Fe^{\scriptscriptstyle ++} + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^{\scriptscriptstyle +}$

 $\mathrm{Cl}^{--} + \mathrm{Fe}^{++} \to \mathrm{Fe}\mathrm{Cl}$

 $FeCl + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+, Cl^{--}$

 $P^{H} = -Log(H^{+})$



Fig. 4.7 Image of created crevice corrosion geometry

4.6.5 Input data for simulation

Fig. 4.8 shows the potentiodynamic polarization curve which was used to simulate the crevice corrosion. The potentiodynamic polarization curve consists of active and passive region, where current density magnitude increases in the active region with the increased anodic polarization but in the passive region, current density decreases with the increase polarization. The input data are listed in Table 4.2 that's used during the simulation.



Fig. 4.8 Polarization data for the HEA electrode reaction for a potential scan in the active- to-passive direction.

Table 4.	2
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Description	Values
Electrolyte conductivity	10 (S/m)
Polarization voltage(V_pol)	0.5(V)
Density of HEA	7931.9(kg/m ³)
Molar mass of HEA	0.33125(kg/mol)
Temperature	25(°C)
Equilibrium potential	0
Electrolyte potential	0
Kinetics expression type (local	i_alloy(A/cm ²)
current density)	
Number of electron participating	15

Chapter: 5

Result and discussion

5. Characterization of HEAs

The structure and phase evolution of multicomponent HEAs is identified by XRD and SEM coupled with EDS. The brief analysis of microstructure of HEAs is given in this chapter to understand the phase equilibria.

5.1 Structural Characterization

The structural characterization of HEAs was carried out using X-ray diffraction (XRD) (Panalytical X-pert pro instrument) with Cu-K_{α} (λ = 0.154056 nm) radiation, operated at 45kV and 30mA, with the step size 2θ = 0.017 degree. The International Committee for Diffraction Data (ICDD) database was used in PCPDFWIN software to identify the peaks in the XRD The XRD of multicomponent Fe₃₅₋ pattern. patterns _vCo₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr_v HEAs series are shown in Fig. 5.1 to understand the structural characterization behavior. It is to be noted that the XRD patterns show the different intense diffraction peaks w.r.t. different zirconium (Zr) in investigated HEAs. The XRD pattern of HEAs shows a single FCC 12 solid solution phase with the zirconium (Zr = 0 at. %), while XRD pattern of HEA with Zr = 2 at. % shows another Laves phase along with the solid solution FCC_12 phase. Further on the addition of zirconium contents up to 4 at. %, XRD pattern shows again FCC_12 solid solution phase and Laves phase (MnZr type). The XRD pattern of HEAs with Zr = 8, 10 at. % gives one another intermetallic phase (Ni₇Zr₂ type) along with FCC_12 solid solution phase and Laves phase.



Fig 5.1 XRD Pattern of multicomponent $Fe_{35-y}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_y$ (y= 0, 2, 4, 6, 8, 10) HEAs.

5.2 Microstructural characterization

The Microstructural Characterization of the samples was examined by scanning electron microscopy (SEM) and compositional analysis was done by energy dispersive spectroscopy (EDS). The microstructure of multicomponent HEA reveals the presence of primary FeCoNiCr-rich solid solution phase (FCC_L12) with light gray contrast, as shown in Fig. 5.2 (a), and The lower magnification SEM micrograph shows porosity in the single-phase microstructure.

The microstructure of HEA with Zr = 2 at. % shows two different phases, as shown in Fig. 5.2 (b), The name of phase is marked as **phase(A)** and **Phase(B).** The phase(A) gives FCC solid solution phase and Phase(B) shows eutectic mixture. The Phase(B) having FeCoNiCr-rich solid

solution phase (FCC_L12) and MnZr type Laves phases having dark contrast in Fig. 5.2 (b). The composition analysis of each phase was done by using EDS mapping, which is listed below in Table 5.1. According to thermodynamic reaction, the liquid undergo eutectic reaction to form both FCC and Laves phase i.e. $L = FCC_L12 + MnZr$



Fig. 5.2 BSE-SEM micrograph of multicomponent $Fe_{35-y}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_y$ HEAs; (a) y = 0 and (b) y= 2

Table	5.1	
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Sample	Phase	Fe(at%)	Ni(at%)	Cr(at%)	V(at%)	Co(at%)	Mn(at%)	Zr(at%)
	Phase(A)	35.41	23.5	15.59	10.72	10.40	4.31	0.12
Y=2	Phase(B)	32.01	25.90	13.52	15.52	10.34	4.77	0.94
	Nominal	33	25	15	10	10	5	2

It is important to note here that the volume fraction of eutectic phase in the microstructure increases with the increase in Zr content in HEAs, as shown in Fig 5.3. The microstructure shows primary phase FCC solid solution phase and eutectic mixture with the addition of zirconium (Zr = 4 at.%) contents. The eutectic microstructure shows FeCoNiCr-rich phase and the MnZr type Laves phase and also having higher amount of zirconium contents than the nominal EDS composition as listed in Table 5.2 The zirconium (Zr = 6 at. %) HEA sample are also showing similar result as HEA with Zr = 4 at. %, which is shown in Fig. 5.3 (b) and the EDS results, is listed in Table 5.3.



Fig. 5.3 BSE-SEM Micrograph of multicomponent Fe₃₅₋ $_{y}Co_{10}Ni_{25}Mn_{5}Cr_{15}V_{10}Zr_{y}$ HEAs; (a) y= 4, (b) y= 6.

Table 5.2

Sample	Phase	Fe(at%)	Ni(at%)	Cr(at%)	V(at%)	Co(at%)	Mn(at%)	Zr(at%)
	Phase(A)	37.94	23.11	11.76	11.45	11.08	4.47	0.18
Y=4	Phase(B)	26.68	30.10	8.30	9.53	10.26	5.43	9.70
	Nominal	31	25	15	10	10	5	4

Table 5.3

Sample	Phase	Fe(at%)	Ni(at%)	Cr(at%)	V(at%)	Co(at%)	Mn(at%)	Zr(at%)
	Phase(A)	35.01	16	21.73	13.55	9.56	4.08	0.06
Y=6	Phase(B)	30.55	24.43	15.20	11.31	10.65	4.11	3.75
	Nominal	29	25	15	10	10	5	6

Fig. 5.4 (a) shows SEM micrograph of HEA with Zr=8 at. %, which reaveals the presence of three different phases, as marked as Phase(A), Phase(B) and Phase(L). The light contrast phase having Zr-rich (C_15 Laves) and FCC_12 solid solution phase, which is marked by the Phase(L) in the microstructure, and Phase(A) is FeCoNiCr-rich FCC solid solution phase. The eutectic mixture shows the combination of FCC solid solution phase and intermetallic. The compositions of phase are listed in Table 5.4 and 5.5.

It is important to note that the microstructure of HEA with Zr = 10 at. % shows fully eutectics, as shown in Fig. 5.4 (b), and is observed that formation of eutectic mixture continuously increases with the addition of Zr content in investigated HEAs.

Fig. 5.4 BSE-SEM Micrograph of multicomponent Fe₃₃₋ $_{y}Co_{10}Ni_{25}Mn_{5}Cr_{15}V_{10}Zr_{y}$ HEAs; (a) y= 8, (b) y= 10

Table 5.4

Sample	Phase	Fe(at%)	Ni(at%)	Cr(at%)	V(at%)	Co(at%)	Mn(at%)	Zr(at%)
	Phase(A)	33.08	14.59	21.70	15.75	16.97	9.46	4.05
Y=8	Phase(L)	16.37	38.91	4.95	2.86	10.12	5.54	21.25
	Phase(B)	32.01	14.84	22.61	14.21	9.60	3.90	2.82
	Nominal	27	25	15	10	10	5	8

Table 5.5

Sample	Phase	Fe(at%)	Ni(at%)	Cr(at%)	V(at%)	Co(at%)	Mn(at%)	Zr(at%)
	Phase(B)	29.42	24.38	14.65	9.98	10.63	3.76	7.18
Y=10								
	Nominal	25	25	15	10	10	5	10

5.3 Thermodynamic parameter

Both thermodynamic and Hume-Rothery parameter were calculated for the multicomponent HEAs, which is listed in Table 5.6 and 5.7. The enthalpy of mixing (ΔH_{mix}) increases with increase of zirconium content and hence increase the tendency for the formation of intermetallic in the HEAs. The negative values of Gibbs free energy (ΔG_{mix}) shows the formation of stable phase in the HEA at room temperature. It was also observed that the mixing entropy, ΔS_{mix} values increases with addition of zirconium content in the alloy. The tendency of formation ordered intermetallic phase in the HEA increases on the increasing of ΔH_{mix} and similarly tendency for formation of disordered phase increases on the increasing ΔS_{mix} .

According to Table 5.7, the effect of Ω was utilized to compare both (Δ Hmix) and (Δ Smix) parameters, and found that entropy is main parameter which play vital role for the formation of solid solution in the HEA, and also observed, the values of term Ω continuously decreases with the increase of zirconium content in alloy, and also observed from the table that the effect of (Δ Hmix) is predominant as compared to mixing of entropy in the alloy during formation of intermetallics.

The melting temperature of the HEAs was calculated by using mixture rule and found that the melting temperature of the HEAs increases with increase of zirconium content. It is to be noted that the minimum values of atomic size difference (δ) leads to the formation of FeCoNiCr type solid solution, and also observed that the formation of intermetallics increases with increase values of atomic size difference (δ). The intermetallic formation tendency increases with the addition of zirconium content and decreases the formation of solid solution phases in the HEA. Another Hume-Rothery parameter electronegativity difference ($\Delta \chi$) which leads to
the formation of single solid solution phase due to lowering value, Similarly, the valence electron concentration (VEC) factor signifies the formation of FCC solid solution phase in the HEAs, and also observed that the formation of intermetallic increases continuously with the addition of zirconium content in the alloy. A new parameter Λ was introduced through the combine effect of atomic size difference (δ) and mixing entropy (ΔS_{mix}), and shows the maximum value for the multicomponent Fe₃₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₀ HEA, as listed in Table 5.7. It is also to be noted that eutectic phase mixture formation increases with the addition of zirconium content which could be attributed to the minimum value of Λ .

Thermodynamic parameter

Table 5.6

Alloy	ΔH_{mix}	ΔS_{mix}	ΔG_{mix}	T _m (K)
$Fe_{35}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_0$	-6.260	13.373	-24.925	1863.40 K
$Fe_{33}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_2$	-8.404	14.011	-26.205	1869.74 K
$Fe_{31}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_4$	-9.736	14.407	-27.038	1876.08 K
$Fe_{29}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_6$	-12.284	14.706	-27.695	1882.42 K
$Fe_{27}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_8$	-13.700	14.937	-28.226	1888.76 K
$Fe_{25}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_{10}$	-15.900	15.113	-28.655	1895.10 K

Table 5.7

Hume-Rothery parameters

Alloy	δ (%)	VEC	Ω	Δχ	Λ
$Fe_{35}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_0$	2.3904	7.95	3.980	0.1136	2.3403
$Fe_{33}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_2$	5.0817	7.87	3.117	0.1308	0.5425
$Fe_{31}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_4$	5.8197	7.79	2.776	0.1453	0.4253
$Fe_{29}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_6$	6.8160	7.71	2.253	0.1579	0.3165
$Fe_{27}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_8$	7.6281	7.63	2.059	0.1689	0.2567

$Fe_{25}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_{10}$	8.3011	7.55	1.801	0.1788	0.2193

5.4 Model validation of HEA

The input data used for the model validation of HEA, is shown in Table 5.8

Table 5.8:

Property	Values	units
Equilibrium potential	-0.5584	V
Current density of HEA	1.850×10 ⁻⁵	A/m ²
Anodic transfer coefficient (α_a)	158.353	mV
Cathodic transfer coefficient (α_c)	105.196	mV
Density of HEA	7931.9	Kg/m ³
Molar mass of HEA	0.33125	Kg/mol
σ Conductivity of electrolyte	10	S/m
Electrolyte potential	0	V
Surface length of HEA	30	mm
Width of HEA sample	20	mm
Thickness of HEA sample	2.5	mm

Utilization of (B-V) relationships for the potential.

5.4.1 Potential in the electrolyte

The Butler-Volmer (B-V) relations were applied at the electrode surface, and obtained the distribution of potential in the electrolyte; as shown in Fig. 5.5 and 5.6. The electrolyte potential varies from 0 to 2.8×10^{-6} V along the electrode surface and the arrow shows the distribution of current density. The maximum electrolyte potential is found near the anode surface and minimum (zero) in the blue-color zone.



Fig. 5.5 Describes the distribution of potential in the electrolyte along the electrode surface of the HEA.



Fig. 5.6 1D plot of electrolyte potential along the electrode surface for HEA.

5.4.2 Electrolyte current density

The streamlines show the distribution of current density in the electrolyte as shown in Fig. 5.7. The result shows maximum current density in the electrolyte is 3×10^{-3} and minimum of 9.68×10^{-5} Am⁻².



Fig. 5.7 Describes the distribution of current density in the electrolyte along the electrode surface for HEA.

5.4.3 Electrode potential

The magnitude of electrode potential was measured in the electrolyte with a reference electrode which shows the range of potential. Fig. 5.8 (a) and (b) shows the maximum electrode potential of 2.29×10^{-6} V and minimum electrode potential of 2.8×10^{-6} V.



Fig. 5.8 (a) and (b) Describes the distribution of electrode potential with the reference electrode for HEA.

5.5 Crevice corrosion

The distribution of potential in the electrolyte result obtained from the simulation by using Comsol multiphysics software. The maximum electrolyte potential towards the crevice tip and minimum at the crevice mouth is estimated, as shown in Fig. 5.9. The measured magnitude of

maximum electrolyte potential is 40.2 mV and minimum 0 mV for 0 hour. Fig. 5.10 shows the surface distribution of potential in the electrolyte for the time period t = 50 hour, and measured 44.8 mV maximum electrolyte potential at the end of crevice tip. 1-D diagram of electrolyte potential for various time periods are plotted to better understand the distribution for a time period range 0 to 50 h. It is observed that the magnitude of potential distribution is increasing towards the crevice tip, and decreasing towards the crevice mouth. The electrolyte potential distribution is shown in Fig. 5.11 for the time period t = 0, 10 h, 20 h, 30 h, 40 h and 50 hour.



Fig. 5.9 Surface plot of potential distribution in the electrolyte for HEA at time t = 0 h.



Fig. 5.10 Surface plot of potential distribution in the electrolyte for HEA at time t = 50 h.



Fig. 5.11 1-D plot of electrolyte potential Vs crevice depth for HEA at various times.

Fig. 5.12 shows the distribution of electrode potential for the time period t = 50 hour. The maximum potential was measured 0.54 V near the crevice tip, and minimum away from the crevice tip, that is 0.5 V. The 1-D plot of electrode potential shows the results for the different time periods, as shown in Fig. 5.13. It is observed that the electrode potential increases towards the crevice tip.



Fig. 5.12 Surface plot of electrode potential for HEA at time t = 50 h



Fig. 5.13 1D plot of Potential vs. crevice depth for fixed gap for different periods.

Fig. 5.14 shows the current density distribution for the various time periods, and observed that the current density decreases towards the crevice tip and increases away from the crevice tip. The maximum current density of 7.5 (A/m^2) near the crevice mouth is obtained and also observed that the current density distribution graph overlap at x = 0 mm for each time period.



Fig. 5.14, Total or local current vs. depth plot for fixed gap at various periods.

Fig. 5.15 shows the damage profile of the HEA for the time period (t = 50 h), and observed that the maximum profile damage between in the range (x = 0 to 1 mm). It is found that 120 μ m maximum and 109 μ m minimum values of damage profile is obtained. 1-D diagram is plotted for the better understanding behavior of the damage profile, as shown in Fig. 5.16. It is observed that the maximum deformation is due to availability of maximum current density in the range (x = 0 to 1 mm), as shown in Fig.5.14. Therefore, thickness profile on the surface of HEA for the different time period is obtained. It is observed that there is 0 mm damage profile at time t = 0 hour, 0.03 mm at t = 10 hour, 0.055 mm at t = 20 hour, 0.082 mm at t = 30 hour, 0.11 mm at t = 40 hour and 0.13 mm at t = 50 hour.



Fig. 5.15 Surface plot of damage profile (mm) for HEA at time t = 50 h



Fig. 5.16 1-D plot of damage profile (mm) Vs crevice depth (mm) for HEA at different periods.

Fig. 5.17 shows the distribution of current density in the electrolyte. The maximum current density distribution is obtained near the crevice mouth at a distance (x = 0 mm), and minimum at the crevice tip (x = 15 mm). The maximum value of current density 49.8 (A/m^2) and minimum 1.26 (A/m^2) for time (t = 50 hour) is measured. Fig. 5.18 shows 1-D plot of current density distribution for the various time periods. It is observed that

magnitude of current density in the electrolyte decreases towards the crevice tip and increases near the crevice mouth for the time period t = 0, 10, 20, 30, 40 and 50 hours.



Fig. 5.17 Surface plot of current distribution in the electrolyte for HEA at time t = 50 h



Fig. 5.18 1-D plot of electrolyte current density Vs crevice depth for HEA at various times.

5.6 Polarization curve

The potentiodynamic polarization of both curves Fe₃₅Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr₀ (HEA) and SS316 are shown in Fig. 5.19 and their electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}) and break-down potential (E_{bre}) are listed in Table 5.9 and 5.10. The polarization curve of HEA and SS316 are not overlapping each other, therefore showing almost unlike corrosionresistant behavior. The SS316 polarization curve shows lower current density (i_{corr}) with higher corrosion potential (E_{corr}) as compared to the HEA. Therefore, multicomponent of (HEA) has lower corrosion resistance than the SS316 stainless steel which could be attributed to the improper distribution of protective alloying elements.



Fig. 5.19 Polarization behavior of HEAs and SS316

The i_{corr} was obtained corresponding to E_{corr} from the potentiodynamic polarization plots. The E_{corr} is found to be 558.4 mV (SCE) and 327.8 mV (SCE) for HEA and SS316 respectively, as shown in Fig.5.25. The corrosion current density (i_{corr}) and corrosion rate are reported for both HEA and stainless steel, as listed in Table 5.10. The corrosion current density is a critical parameter that is used to estimate the corrosion rate with the help of Faradays law.

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Sample	Instrument Model	Open circuit potential(V)	Initial potential E(V)	Final potential E(V)
316 SS	CHI604E	-0.3234	-0.5	0
HEA	CHI604E	-0.5277	-0.75	-0.25

Table 5.10

Sample	Designation	E _{corr} (mV)	I _{corr} (µA/cm²)	Corrosion rate (mmpy)	Scan rate(V/s)
$Fe_{35} Co_{10} Ni_{25} Mn_5 Cr_{15} V_{10} Zr_0$	Zr ₀	558.4	18.50	0.0763	0.001
Stainless Steel	316	327.8	2.346	0.0527	0.001

Chapter: 6

Summary

The aim of this project is to develop the HEAs by using thermodynamic simulation technique, and study the corrosion behavior of multicomponent Fe_{35-v}Co₁₀Ni₂₅Mn₅Cr₁₅V₁₀Zr_y HEAs. The samples were prepared in the vacuum arc melting cum casting unit under the argon atmosphere, followed by microstructural characterization, structural characterization The and corrosion experiment. XRD. EDS composition and thermodynamic simulation was utilized to evaluate the phase evolution and to establish the phase equilibria. The corrosion experiment of the HEA and stainless steel (SS316) is carried out using NaCl (electrolyte). The corrosion rate of HEA and SS316 are evaluated after performing galvanic corrosion experiments, and also compared the corrosion rate of HEA with the corrosion rate of SS316. The sample was dipped for the 5 days in the electrolyte solution before the experiment, and the Tafel data was used to determine the simulation. The simulation of galvanic corrosion and crevice corrosion was done using Comsol multiphysics software to understand the distribution of potential and current density in the electrolyte medium.

Scope for future work.

1. To study the corrosion behavior of multicomponent $Fe_{35-y}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_y$ HEA for (Zr = 0, 6) % in the different electrolyte solution such as HCl, H2SO4, NaOH and HNO3 for the different time periods.

2. To study the corrosion behavior of stainless steel (SS316), and compared this with the studied HEA.

3. To study the mechanical behavior, especially hot deformation behavior of $Fe_{35}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_0$ and $Fe_{29}Co_{10}Ni_{25}Mn_5Cr_{15}V_{10}Zr_6$ HEAs.

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