SYNTHESIS AND CHARACTERISATION OF (Fe-Cr-Cu-Co-Ni-Si) EUTECTIC HIGH ENTROPY ALLOYS

THIS REPORT IS SUBMITTED IN THE FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF **BACHELOR OF TECHNOLOGY**

IN

METALLURGICAL AND MATERIALS ENGINEERING

BY

ABHISHEK PASWAN
(ROLL NO-15120003)

PRADEEP PRASAD
(ROLL NO-15120053)

SATYAKI CHAKRAVORTY
(ROLL NO-15120065)

YAGYAVAL SINGH RAJPUT
(ROLL NO-15120082)

GUIDED BY:

Dr MANOJ KUMAR CHOPKAR

NATIONAL INSTITUTE OF TECHNOLOGY, Raipur (CG)

2018-19

DECLARATION

This project work is a presentation of our original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussion.

The work had been done under guidance of **Dr Manoj Kr Chopkar, Department of Metallurgical Engineering, National Institute of Technology, Raipur** .The result embodied in this report, in full or in parts, has not been submitted elsewhere for the award of any degree or diploma

ABHISHEK PASWAN
(ROLL NO-15120003)

PRADEEP PRASAD
(ROLL NO-15120053)

SATYAKI CHAKRAVORTY
(ROLL NO-15120065)

YAGYAVAL SINGH RAJPUT
(ROLL NO-15120082)

In my capacity as a supervisor of this project work, I certify that the above statements are true to the best of my knowledge.

Dr Manoj Kumar Chopkar

ASSISTANT PROFESSOR

NATIONAL INSTITUTE OF THECHNOLOGY

RAIPUR

CERTIFICATE

This is to certify that this project work entitled **"Synthesis and Characterisation of Eutectic High Entropy Alloys"** submitted by **YAGYAVAL SINGH RAJPUT(15120082), SATYAKI CHAKRAVORTY (15120065), PRADEEP PRASAD (15120053)** and **ABHISHEK PASWAN(15120003)** in partial fulfilment of the requirements for the award of **BACHELOR OF TECHNOLOGY** degree in **Metallurgical Engineering** at **National Institute of Technology, Raipur** is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

Date: 09th MAY, 2019

Dr **Manoj Kumar Chopkar**

Dept. of Metallurgical Engineering,

National Institute of Technology Raipur, C.G.

CERTIFICATE OF APPROVAL

This is to certify that the project entitled "**Synthesis and characterisation of eutectic high entropy"** submitted **YAGYAVAL SINGH RAJPUT(15120082), SATYAKI CHAKRAVORTY (15120065), PRADEEP PRASAD (15120053)** and **ABHISHEK PASWAN(15120003)** to the Department of Metallurgical Engineering, National Institute of Technology Raipur, for the partial fulfilment of the requirements for the award of the **Bachelor of Technology** in **Metallurgical Engineering** has been accepted and that the students have successfully defended the project in the viva voce examination.

Date: 9th May, 2019

Dr**. Manwendra Kumar Tripathi**

Head, Department of Metallurgical Engineering
National Institute of Technology, Raipur

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ABHISHEK PASWAN(ROLL NO-15120003)
PRADEEP PRASAD(ROLL NO-15120053)

SATYAKI CHAKRAVORTY(ROLL NO-15120065)
YAGYAVAL SINGH RAJPUT(ROLL NO-15120082

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ABSTRACT

Recently, High Entropy Alloys are found to be a good candidate for high-temperature applications due to its attractive high-temperature properties but there is a compositional inhomogeneity and weak castability . To get rid of these problems eutectic high entropy alloys have been developed in recent years. Currently, people have developed the **HEA** CoCrCuFeNi, but the effect of Si addition on these alloys and its effect on various mechanical properties and the phase evolution is still unclear. In this current work, we have synthesised the novel **$CrCuFeCoNi_{2.1}Si_{0.55}$**, **$CrCuFeCoNi_2Si$** and **CrCuFeCoNiSi** by vacuum arc melting method. The characterisation of phase evolution by OM , SEM and XRD is done and physical characteristics are evaluated via microhardness, corrosion behaviour.

Keywords- Eutectic high-temperature alloys, Si addition, vacuum arc melting, characterisation

Abbreviations-1**)** HEAs-High Entropy Alloys
2) EHEAs-Eutectic High Entropy Alloys
3) OM-Optical Microscope
4) SEM-Scanning Electron Microscope
5) XRD- X-Ray Diffraction

CHAPTER 1

INTRODUCTION

INTRODUCTION

High Entropy Alloys are a new class of advanced materials in which it is designed on the basis of mixing all the elements in equiatomic or near equiatomic proportions. These alloys show excellent room and high-temperature properties due to the following mechanisms- high configurational entropy, sluggish diffusion leads to excellent phase stability at high temperatures, large lattice distortion due to the interaction between various elements added in equiatomic proportions and cocktail effect which shows composite like properties.

The problem with HEAs is they either show very high strength i.e. brittle due to the presence of BCC phase or they show very high ductility i.e. soft due to the presence of FCC phase and also single phase HEAs shows very high segregation due to the presence of multiple elements, poor castability and poor high-temperature properties. To resolve these problems eutectic high entropy alloys have been developed. As compared to the conventional HEAs these alloys show good castability and high-temperature properties due to the presence of a hard intermetallic compound in them which suppresses the oxidation behaviour at high temperature.

Designing of EHEAs based on Pseudo binary strategy and Valence electron Concentration has been employed to design these alloys. Earlier approaches used to design these alloys were to take the CoCrFeNi series and elements were added in this series to obtain the desired mechanical properties. Similarly, many alloys were developed on the basis of these series but no one has proposed the effect of Si addition on the alloying behaviour and mechanical properties of the materials.

Table 1: Mixing enthalpy (kJ/mol) of the binary of constituent elements calculated by Miedema's model [12]

Elements	Si	Cr	Fe	Co	Ni	Cu
Si		-37	-35	-38	-40	-19
Cr			-1	-4	-7	12
Fe				-1	-2	13
Co					0	6
Ni						4
Cu						

Table 1 shows that due to high negative mixing enthalpy between Si and Ni an intermetallic was formed and due to negative mixing enthalpy between other elements a single-phase FCC was formed.

Recently **$CrCuFeCoNi_{2.1}Si_{0.55}$, $CrCuFeCoNi_2Si$ and CrCuFeCoNiSi** alloys were developed in our lab by a mechanical alloying method which was done by carrying ball milling for 20 hours. After synthesis of these alloys, an intermetallic compound of Ni_3Si has been found in the matrix of FCC which has been confirmed by the XRD and EDX but the possibility of the eutectic structure has not been detected but it was predicted that eutectic structure may be obtained in the cast EHEAs. To confirm this behaviour the experimentation is carried out and the behaviour is reported in this present paper.

The objective of this present work is to investigate the microstructure behaviour and the mechanical and corrosion properties of these alloys. The EHEAs were synthesised by Vacuum arc melting method route. In these the pellets, each of weight 10 grams was made by compaction and overall 3 pellets of 30 grams were melted in vacuum arc melting furnace to obtain the hemispherical-shaped sample. After preparing the alloys they were characterised by OM, SEM and XRD to confirm the presence of the eutectic structure in the alloys. After characterisation, the properties of the alloys will be tested by Compression testing, Microhardness testing, dry Wear behaviour and finally the corrosion behaviour.

CHAPTER 2:

LITERATURE REVIEW

LITERATURE REVIEW

In order to understand the previous research work done on the HEAs and to implement our ideas on the field of HEAs various research papers have been studied. Here we have reported the literatures and citations reviewed by us before experimentation.

1. A pseudo binary strategy was proposed to design eutectic high entropy alloys using mixing enthalpy and valence electron concentration;

2. An eutectic high entropy alloy can be obtained by mixing a stable FCC-structured solid solution and a stable IMC;

3. Three eutectic high entropy alloys were successfully prepared using this strategy;

4. All the three alloys exhibited excellent mechanical properties, with tensile fracture strength >1000MPa and elongation> 12%.

CHAPTER 3:

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

In this present work the pure elemental powders of purity >99.5% is taken and it is mixed manually in the desired ratio to obtain the nominal composition of the alloy. The alloys of different compositions are tabulated below-

Sample No.	Alloy	Cr atomic %	Cu atomic %	Fe atomic %	Co atomic %	Ni atomic %	Si atomic %
1	Cr-Cu-Fe-Co-$Ni_{2.1}$-$Si_{0.55}$	14.05	17.2	15.1	15.95	33.3	4.15
2	Cr-Cu-Fe-Co-Ni_2-Si	13.8	16.9	14.85	15.65	31.2	7.45
3	Cr-Cu-Fe-Co-Ni-Si	16.35	20	17.6	18.5	18.5	8.85

Table 2: Nomenclature of alloys and its nominal compositions in atomic %

a. Compaction:

As received premixed powders of alloys were weighed by weighing machine and compacted by die compaction using hydraulic press. Each pellet of weight 3 gm were weighed and 10 pellets of 30 grams were cold compactedbyapplying a load of 600 MPa in a die

of 15 mm diameter. A lubricant (Zinc-Sterate) was used to ensure the easy removal of the compacted cylindrical sample. Similarly, the 30 pellets of desired compositions were made.

b. Vacuum Arc Melting:

The EHEAs alloy pellets of 10 samples of 30 grams were melted by VAR in an Ar atmosphere in water cooled copper hearth under vacuum.The arc melted buttons were re-melted five times to ensure good homogeneity and casted finally to obtain the button shaped product.

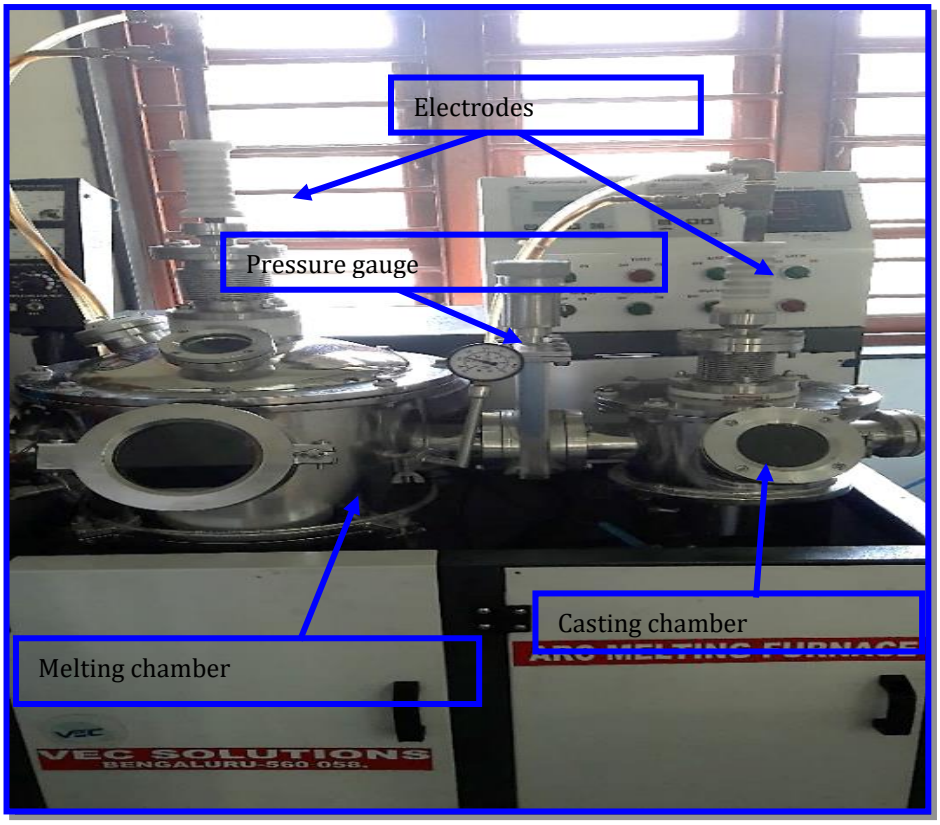


Figure 1: Image of Vacuum arc melting furnace and final product

4.1 Optical Microscope:

The alloys were characterised by the optical microscope after successful synthesis by VAR. The alloys were prepared mechanically

for OM analysis. The steps for preparation of samples for characterisation are described below-

1. Button shaped samples were cut by diamond cutter to obtain a small cylindrical specimen.
2. Cylindrical specimens were grinded on hard SiC rotating wheel to remove the scratches which was made during cutting.
3. Cut specimens were polished on belt grinder to dissolve the coarse lines made during coarse grinding.
4. All the specimens were polished on emery paper of designation 1/0, 2/0, 3/0, and 4/0 respectively changing the direction of polishing about 90° after every operation under a given paper for efficient removal of scratches on the surface.
5. Polished specimens were cloth polished to obtain clean mirror like finish. Diamond paste was used as a lubricant during polishing on Laplace cloth.
6. Specimens were etched in marbles reagent (4 g of copper sulphate in 20 mL of hydrochloric acid and 20 mL of water) for 5 seconds. The optical micrographs were obtained. Images were taken under bright mode in of Zeiss Axio Lab A1 microscope.

Figure 2: Optical microscope in our lab

4.2 XRD Analysis-

The XRD analysis was carried out for all the samples to confirm the type of phases present in the samples. It was done using X-ray Diffractometer(Panalytical, X′ pert powder).The scan range was kept 0.5counts per second and 2 theta is set for 20-90º.

Figure 3 XRD analyser

4.3SEM analysis-

The samples obtained from the XRD were further characterised in SEM. The preparation includes the same steps as done in the OM and the samples were etched by Marble's reagent(4 g of copper sulphate in 20 mL of hydrochloric acid and 20 mL of water) for 5 seconds. After etching images were taken in secondary electron mode.

Figure 4: SEM with software

4.4 Hardness measurement

The samples were tested by measuring the hardness by Vickers hardness(SIMANDZU Semi-Automatic Micro Vickers hardness tester). In this the load applied was of 10N for a dwell time of 10 seconds. The impression obtained on the specimen was of a square as a result of the shape of the indenter and the length of the diagonals was automatically measured by machine fitted with ocular micrometer and the hardness displayed is in VHN. Minimum 3

hardness values were measured for each sample i.e. 3 for matrix and 3 for intermetallic.

Figure 5: Micro Vickers hardness tester

4.5 Wear analysis

Wear testing of samples were carried out on pin and disc type wear testing machine. The samples were rotated on a steel disc (En-64) of hardness Rc-64 and diameter 50 mm for 5 minutes. The tests were carried out under the following conditions-

1. Load-5Kgf
2. Track diameter-70mm
3. Time- 5 minutes
4. Revolutions- 500 rpm

Test is carried under dry conditions and to avoid contamination the disc was cleaned with clean cloth before testing. The sample preparation includes coarse polishing on emery papers and cleaning with acetone solution.

The parameters are calculated after the test by using these formulas-

1. Sliding speed-N*3.14*D/60
2. Sliding distance-sliding speed*time of revolution
3. Volume loss-final volume-initial volume
4. Wear rate-volume loss/sliding distance
5. Specific wear rate-wear rate/load

4.6 Corrosion test

Corrosion test were performed on samples using potentiostat. For testing samples were grinded mechanically on emery papers and final polishing was done on Laplace cloth using diamond paste. Samples were cold mounted on epoxy to obtain the required exposed area of diameter 3cm. Electrochemical measurements were carried out in an electrolyte of 3.5% NaCl in neutral aqueous solution saturated with atmospheric oxygen. Samples were fixed at one end to expose the surface and cell was filled with 300ml of electrolyte, platinum mesh was used as a counter electrode and a saturated Ag/AgCl electrode as reference electrode. The test was carried out at room temperature and for 1016 points with a fit range of -549.9 mV to 465.8 mV. The corrosion current, Tafel slopes were determined automatically by the software of the machine.

CHAPTER 4

RESULTS AND DISCUSSIONS

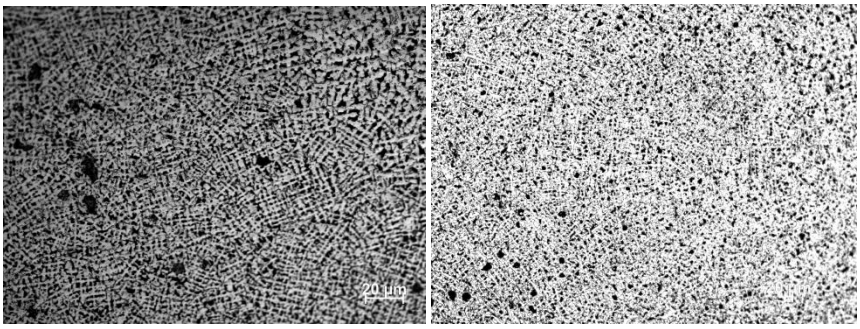
RESULTS AND DISCUSSION

5.1 Microstructures obtained under optical microscope-

The images obtained from the microscope are reported below.

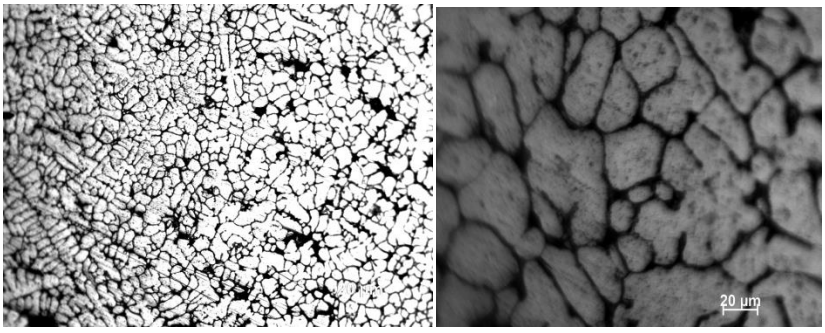
Images of Sample 1: **$CrCuFeCoNi_{2.1}Si_{0.55}$**

Figure 6: Image taken at MAGNIFICATION 50X and 100X



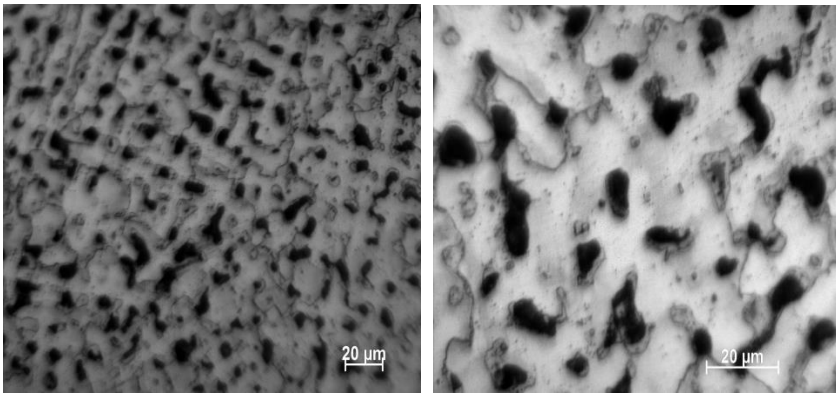
Images of Sample 2: **$CrCuFeCoNi_2Si$**

Figure 7: Image taken at MAGNIFICATION 100X and 500X



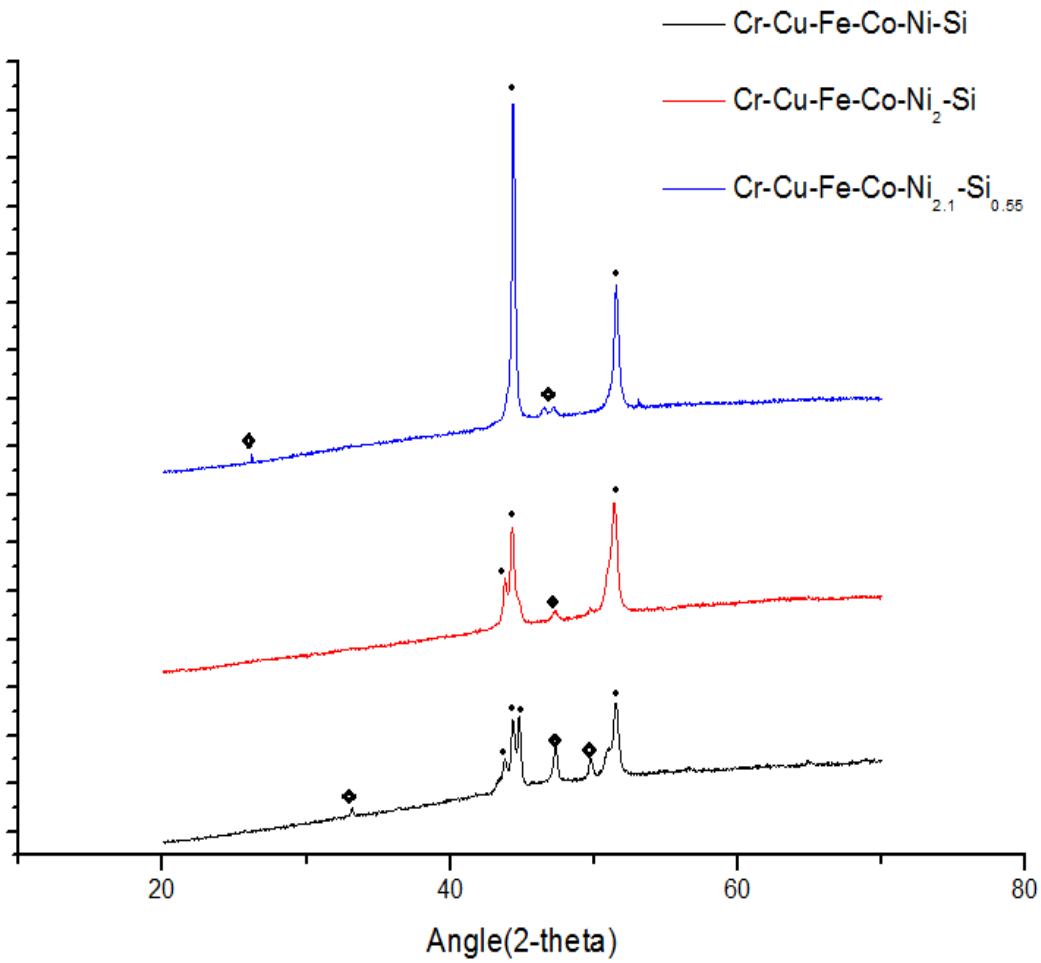
Images of Sample 3: **CrCuFeCoNiSi**

Figure 8: Image taken at MAGNIFICATION 500X and 1000X



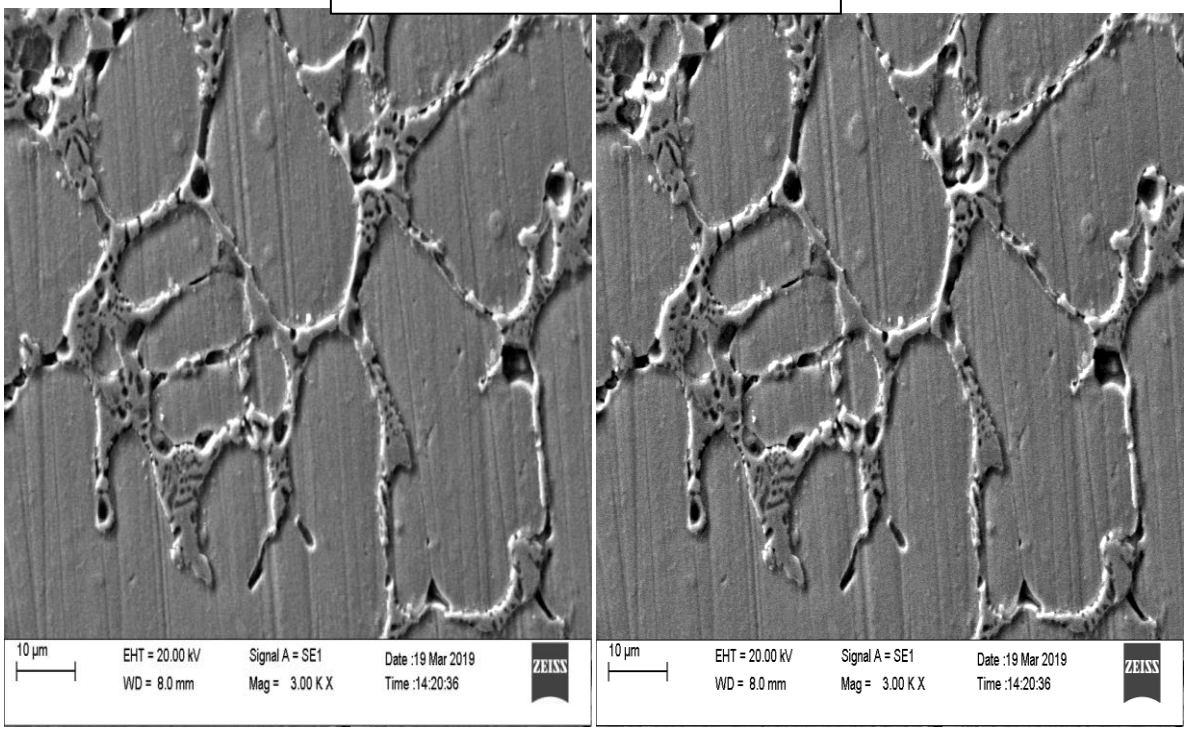
From the images obtained after microscopy it can be said that lamellae has been formed on all the microstructures of samples. Grey area shows the matrix of FCC and a black show the presence of intermetallic which can be further confirmed by SEM and EDX analysis. In the images of Sample 4 dendrites are obtained at the corners due to segregation.

5.2 XRD Analysis



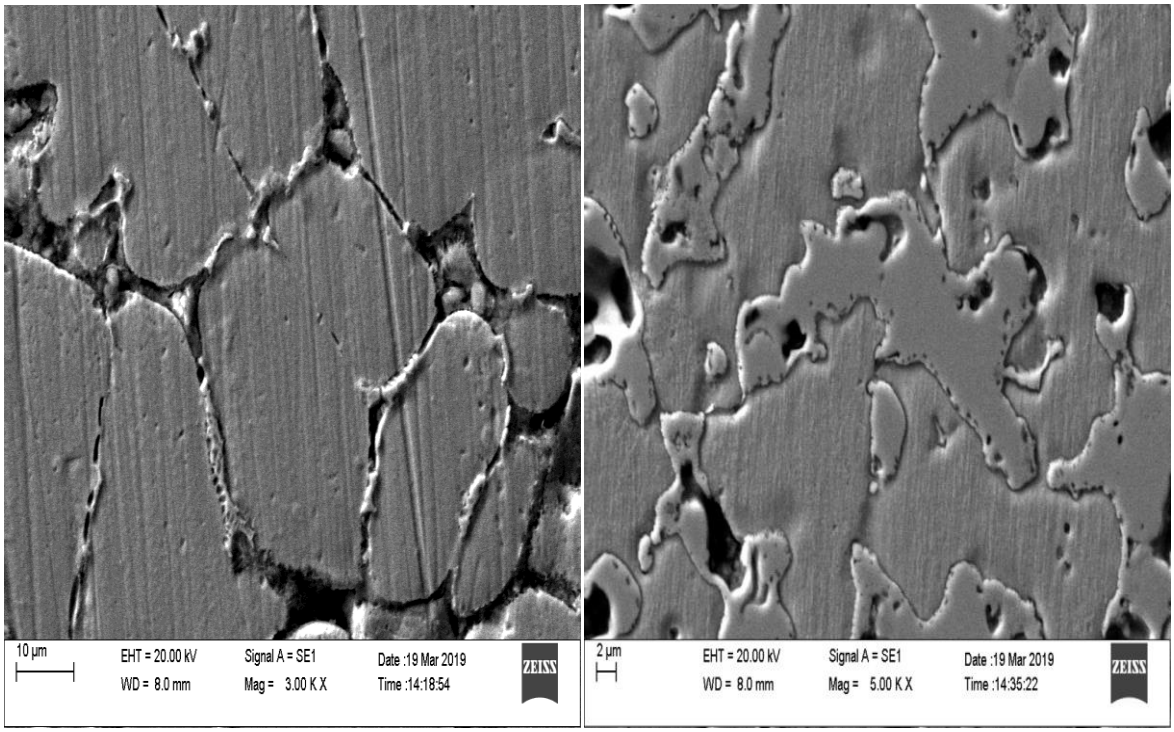
5.3 SEM ANALYSIS

HEA 2 $CrCuFeCoNi_2Si$



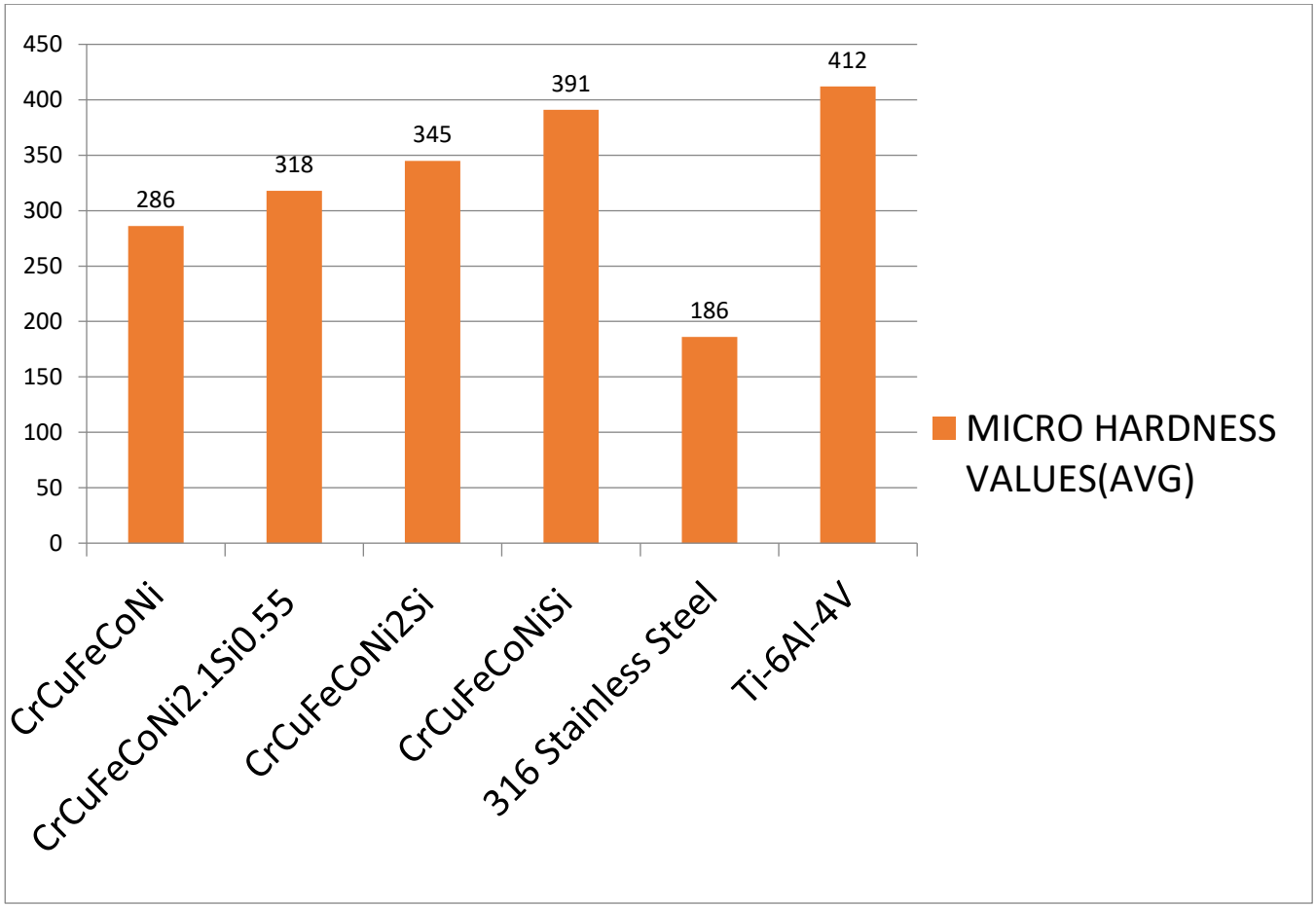
HEA 1 $CrCuFeCoNi_{2.1}Si_{0.55}$

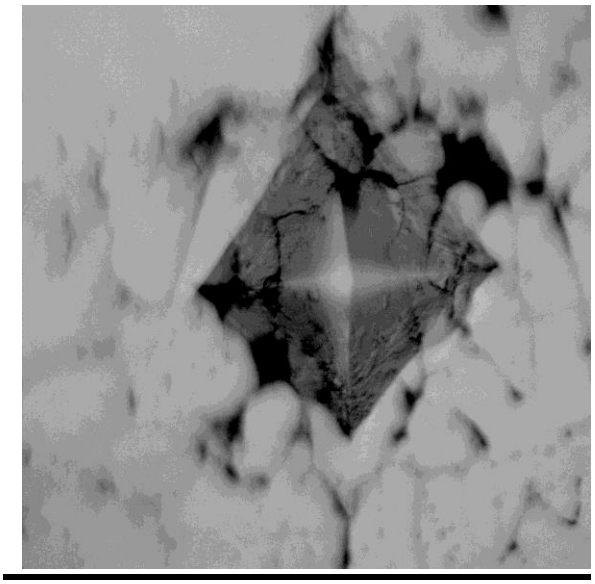
AND HEA 3 CrCuFeCoNiSi



5.4 HARDNESS ANALYSIS

HEA SAMPLE	MICRO HARDNESS VALUES	DWELL TIME(in S)	LOAD (in N)
$CrCuFeCoNi_{2.1}Si_{0.55}$	318	10	9.807
$CrCuFeCoNi_2Si$	345	10	9.807
CrCuFeCoNiSi	391	10	9.807





INDENTATION AFTER HARDNESS

CONCLUSION:

$CrCuFeCoNi_{2.1}Si_{0.55}$, $CrCuFeCoNi_2Si$ and CrCuFeCoNiSi alloy compositions were successfully designed & prepared via vacuum arc melting route.

- **Ni_3Si** eutectic mixture was obtained and verified by SEM, XRD and EDX methods
- The mechanical properties were at par with Titanium alloys, stainless steel in terms of hardness.
- HARDNESS VALUE = 391HV

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