B.TECH. PROJECT REPORT

On Fabrication and Characterization of Eutectic High Entropy Alloys

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Department of Metallurgy Engineering and Materials Science Indian Institute of Technology Indore May 2022

Fabrication and Characterization of Eutectic High Entropy Alloys A PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the degrees

of BACHELOR OF TECHNOLOGY In

Metallurgical Engineering and Materials Science

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CANDIDATE'S DECLARATION

We hereby declare that the project entitled **"Fabrication and characterization of eutectic high entropy alloys"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Metallurgical Engineering and Materials Science' completed under the supervision of **Dr. Ram Sajeevan Maurya from the Department of Metallurgy Engineering and Materials Science,** IIT Indore is an original work. Further, we declare that we have not submitted this work for the award of any other degree elsewhere.

N. B/12 05/22 Vasu 20/05/2022

Signature and name of the students with date

CERTIFICATE by BTP Guide

It is certified that the above statement made by the students is correct to the best of our knowledge.

20.05.2022

Signature of BTP Guide with dates and their designation

Preface

This report on "Fabrication and characterization of eutectic high entropy alloys " is prepared under the guidance of Dr. Ram Sajeevan Maurya from the Department of Metallurgy Engineering and Materials Science, Indian Institute of Technology (IIT) Indore.

Eutectic high entropy alloys (EHEAs) are emerging as a promising new class of structural alloys due to their promising mechanical properties. The development of a fine two-phase eutectic microstructure in HEAs, consisting of a tough phase like fcc and a hard phase like bcc/intermetallic, can aid in achieving an exceptional combination of strength and ductility. Designing eutectic high entropy alloys is a tough task that has previously been attempted using both experimental and theoretical methods. In this work, the potential for eutectic microstructure development of AlCoCrNiV alloy was studied using CALPHAD and manufactured through arc melting. Characterization techniques such as SEM, hardness, and DSC were performed to better understand the structure and properties of the alloy.

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Abstract

High entropy alloys (HEA) are a new class of metals that have proven the ability to outperform traditional alloy systems in terms of physical and mechanical qualities. However, HEAs can have either high strength or high ductility, and achieving both at the same time is still a difficult task. HEA's poor castability and compositional segregation are further impediments to their technological applicability. To address these issues, we presented a technique for designing HEAs based on the eutectic alloy idea. Due to the fine distribution of phases, the development of eutectic microstructure in high entropy alloys can aid in getting an even better combination of mechanical qualities. Using the above-mentioned concept, we designed Al₅(VCr)_{46.36}(CoNi)_{48.64} eutectic high entropy alloy but it did not form eutectic. One possible explanation for this could be the Al content. We need to vary the Al content lower than 5 at% and more than 5 at% systematically to see the eutectic morphology. The DSC too further evidence that there is a large region of melting indicating multiple phases, when observed in SEM micrograph, able to guess that it is a primary FCC followed by some solid-state transformation as indicated by the continuous pores.

Table of Contents	
Candidate's Declaration	
Supervisor's Certificate	
Preface	
Acknowledgements	
Abstract	
1 Introduction	8
2 Objectives	10
3 History of HEAs	14
4 Definition of HEAs	15
4.1 Four core effects	17
5 Experimental results & discussions	
5.1 Thermo-calc results	18
5.2 Vacuum arc melting of the alloy	23
5.3 Metallographic polishing	24
5.4 Differential scanning calorimetry	25
5.5 Scanning electron microscopy with EDS	26
5.6 Vickers Hardness	28
6 Conclusion	29
7 References	30

1. Introduction

In the field of metallic materials, high-entropy alloys (HEAs), also known as multi-principalelement alloys, are emerging as a new study horizon. HEAs are distinguished from typical alloys by the presence of at least five major elements in the ratio of 5 to 35 at%, as opposed to one or two in the conventional alloys. It's a game-changer for alloy design in standard physical metallurgy and unfolds a whole new world of possibilities for novel materials and properties. According to previous research, HEAs have strong softening resistance at high temperatures [1,2] and slow diffusion kinetics [K.-Y. Tsai,2013]. As a result, HEAs are typically recognized as hightemperature materials with great promise. Before HEAs can be substantially pursued for hightemperature applications, a technological obstacle in terms of mechanical property must be overcome. Single-phased HEAs, in general, have found it challenging to strike a suitable compromise between strength and ductility [3,4]. Single-phased HEAs with fcc structure are not strong enough but ductile [5,6]. On the other hand, Single-phased bcc constructed HEAs can be extremely strong but brittle [7]. To our knowledge, no HEAs have been reported to have exceptional balanced strength and tensile ductility. To achieve this balance, a composite approach is expected. However, without a good structural design, just inserting a mixture of bcc and fcc phases will not fix the problem [8]. Furthermore, compositional segregation and poor castability of HEAs, both of which are frequent, degrade their mechanical properties even further, casting a pall over their engineering uses [9,10].

We presented here to employ the eutectic alloy notion to build high entropy alloys with composite structure or to make use of the HEAs conceptualization to construct eutectic alloys, in order to address these key technical challenges that HEAs are now experiencing. We also proposed that eutectic alloys be designed with a combination of hard bcc and soft fcc phases to achieve a balance of high ductility and fracture strength. Eutectic alloys are recognized as a good candidate for high-temperature alloys, in addition to providing a new technique to create the composite form in HEAs, as the solidification structure of eutectic possesses the following features:1) near-equilibrium microstructures that withstand change at temperatures above their reaction temperature; 2) superior creep resistance at high temperatures; 3) programmable microstructures; 4) stable defect

formations; 5) strong rupture strength; 6) low-energy phase borders; 7) in-situ composite formed by the regular rod-like or lamellar eutectic organization. Furthermore, eutectic alloys are believed to be easier to cast. Furthermore, both shrinkage cavities and segregation can be avoided because the eutectic process is an isothermal transition with no solidification temperature range. As a result, if eutectic HEAs having the structure of fcc/bcc composite can be made, they should have the castability and mechanical properties of eutectic alloys, removing barriers to their technological application. Many metallic elements of industrial equipment, like propellers, generator housings, engine housings, adapters, and metal ball valves, are created through direct casting. It is impossible to eradicate casting faults using thermomechanical treatments if the casting quality is insufficient, especially for complicated and big ingots. As a result, the as-cast alloys' casting performance and mechanical qualities are critical for engineering alloys' industrial uses.

Lu et al. advocated using the eutectic-alloy approach to create HEAs, aiming for good castability [11,12], to overcome the above-mentioned challenges for real-world applications of HEAs. They also employed the HEA concept to create eutectic alloys, or the eutectic alloy concept to create HEAs with a composite structure. They also suggested that eutectic alloys be designed with a combination of hard bcc and soft fcc phases to achieve a synergy between high ductility and fracture strength. Since then, the enormous potential of EHEAs in industrial applications and their advantages have enticed a growing number of academics to devote their efforts to EHEA research [11,12]. There are currently more than 100 papers on EHEAs. The AlCoCrFeNi2.1 alloy is the first EHEA to be reported, with a tensile fracture strength of above 1000 MPa, exceptional ductility, and excellent seawater corrosion resistance. This AlCoCrFeNi2.1 alloy has better corrosion resistance and strength than copper alloys [12] used in marine applications, and it has a lower density than copper alloys. As a result, various EHEAs with superior mechanical properties and unique functionality have been discovered. EHEAs have lamellar microstructures, which are fine and regular, and the lamella width usually ranges from a few microns to tens of nanometers. Ordinary solidifications can produce lamellar microstructures which are ultrafine with a lamella width up to 100 nm even in kg-scale casting ingots. The ease with which ultrafine microstructures can be achieved in directly cast alloys is uncommon in conventional alloys, including conventional eutectic alloys. This is due to the growth rate of EHEAs and compositional complexity and the

resultant sluggish elemental diffusion when compared to traditional alloys. Undeniably, a more thorough and comprehensive investigation of the solidification method of EHEAs is required.

2. Objectives

- To develop novel design methodology to predict eutectic composition in high entropy alloys using ThermoCalc software
- Fabrication of Eutectic High Entropy Alloys
- Characterisation of eutectic high entropy alloys
- > Mechanical properties evaluation of eutectic high entropy alloys

In a binary eutectic alloy, solidification of the eutectic alloy is normally accomplished through the reaction of $L \rightarrow \alpha + \beta$, where L represents the liquid phase and, α and β represent the separate phases. Table 1 summarizes the EHEAs with totally eutectic microstructures that have been reported. All documented EHEAs with totally eutectic microstructures have a two-phase structure, while three-phase EHEAs are yet to be described, which is considerably different from standard eutectic alloys. This anomaly could be explained by EHEAs' intricate solidification mechanism and difficulties with coupling and diffusion, which limit the creation of ternary eutectic phases, implying that EHEAs' solidification mechanism has to be investigated further.

Nos	Alloys	Morphology	eutectic structure	References
1	AlCoCrFeNi2.1	eutectic	(FeCoCr)-FCC + (AlNi)-B2	[11]
2	Al1.2CrCuFeNi2	eutectic	(FeCr)-FCC + [(NiCu)Al]CrFe)-B2	[13]
3	Co30Cr10Fe10Al18Ni32	eutectic	FCC+BCC	[14]
4	AlCrFeNi3	eutectic	(FeCrNi)-FCC + (AlNi)-B2	[15]
5	AlCoo.2CrFeNi2.8	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[15]
6	AlCoo.4CrFeNi2.6	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[15]

7	AlCoo.6CrFeNi2.4	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[15]
8	AlCoo.8CrFeNi2.2	eutectic	(FeCoCrNi)-FCC + (AlNi)-B2	[15]
9	CrFeNi2.2Alo.8	eutectic	(FeCrNi)-FCC + (AlNi)-B2	[16]
10	Al16Co41Cr15Fe10Ni18	eutectic	(FeCoCrNi)-FCC + (AlNi)- rich BCC	[17]
11	Ni30Co30Cr10Fe10Al18W2	eutectic	(FeCoCrNi)-FCC + (AlNi)- rich B2	[18]
12	CoCrFeNiZr0.5	eutectic	(FeCoCr)-FCC+Zr-rich Laves	[19]
13	CoCrFeNiTa0.395	eutectic	(FeCr)-FCC + Ta-rich Laves	[20]
14	CoCrFeNiMnPd0.6	eutectic	(CoCrFeNiMn)-FCC + MnxPdy	[21]
15	CoCrFeNiMnPd	eutectic	(CoCrFeNiMn)-FCC + MnxPdy	[21]
16	CoCrFeNiMnPd1.4	eutectic	(CoCrFeNiMn)-FCC + MnxPdy	[21]
17	CoCrFeNiMnPd1.8	eutectic	(CoCrFeNiMn)-FCC + MnxPdy	[21]
18	Co25Fe25Mn5Ni25Ti20	eutectic	(Fe,Co,Ni)-rich FCC+Ti2(Ni,Co)	[22]
19	CoFeNiNb0.5	eutectic	(Fe,Co,Ni)-rich FCC+Nb-rich Laves	[23]
20	V10Cr15Mn5Co10Ni25Fe25.3Nb9.7	eutectic	(Fe,Cr)-rich FCC+Nb-rich Laves	[24]
21	AlCrFeNi	eutectic	(AlNi)-BCC1 + (FeCr)-BCC2	[25]
22	AlCrFeNiMo0.2	eutectic	(AlNi)-BCC1 + (FeCrMo)- BCC2	[25]

23	CoCrFeNiNb0.65	eutectic	(FeCrNi)-FCC + (CoNiNb)Laves	[26]
24	Nb25Sc25Ti25Zr25	eutectic	(Sc,Zr)-HCP + (TiZrNb)-BCC	[27]
25	Ni2FeCoV0.5Nb0.75	eutectic	(FeNiV)-FCC + (CoNb)- Laves	[28]
26	CoFeNiVMo0.6	eutectic	(FeCoNiV)-FCC + CoMo2NiV-type IM	[29]
27	CoFeNi1.4VMo	eutectic	(FeCoNi)FCC + Co2Mo3-type IM	[29]
28	Co2Mo0.8Ni2VW0.8	eutectic	(CoNiV)-FCC + (W,Mo,V)-µ	[30]
29	Al19.3Co15Cr15Ni50.7	eutectic	Al-poor FCC + Al-rich B2	[31]
30	CoCrFeNiMo0.8	eutectic	FCC+Cr9Mo21Ni20-type intermetallic	[32]
31	Fe20Co20Ni41Al19	eutectic	(Fe,Co)-rich L12+(AlNi)-B2	[33]
32	Al1.3CrFeNi	eutectic	(Fe,Cr)-BCC+(AlNi)-B2	[34]
33	Fe28.2Ni18.8Mn32.9Al14.1Cr6	eutectic	(Fe,Mn,Ni)-FCC+(AlNi)-B2	[35]
34	Fe36Ni18Mn33Al13	eutectic	(Fe,Mn,Ni)-FCC+(AlNi)-B2	[36]
35	Fe30Ni20Mn35Al15	eutectic	(Fe,Mn,Ni)-FCC+(AlNi)-B2	[37]
36	AlCrFeNiTi0.25	eutectic	(Fe,Cr)-BCC+(AlNi)-B2	[38]
37	Zr0.6CoCrFeNi2.0	eutectic	FCC+Ni7Zr2	[39]
38	Nb0.74CoCrFeNi2.0	eutectic	FCC+(Co,Ni)2Nb	[39]
39	Hf0.55CoCrFeNi2.0	eutectic	FCC+Ni7Hf2	[39]
40	Ta0.65CoCrFeNi2.0	eutectic	FCC+(Co,Ni)2Ta	[39]
41	CoCrFeNiNb0.45	eutectic	FCC + Laves C15	[40,41]
42	CoCrFeNiTa0.4	eutectic	FCC + Laves C15	[42,41]

43	CoCrFeNiZr0.55	eutectic	FCC + Laves C14	[41]
44	CoCrFeNiHf0.4	eutectic	FCC + Laves C14	[41]
45	Al17Co14.3Cr14.3Fe14.3Ni40.1	eutectic	L12+B2	[42]
46	Al17Co28.6Cr14.3Fe14.3Ni25.8	eutectic	FCC+B2	[42]
47	Al17Co14.3Cr14.3Fe28.6Ni25.8	eutectic	FCC+B2	[42]

Most EHEAs display a lamellar structure. The CoCrFeNiNb0.65 EHEAs' microstructures of the annealed and as-cast states are shown in Fig. 1. The characteristic lamellar structures were found to be stable in samples annealed at 600 and 750 degrees Celsius, which were the same as those discovered in the as-cast alloy. The three alloys have lamellar spacings of 0.25, 0.22, and 0.44 m, respectively. The eutectic grain size coarsened slightly after annealing. However, considerable spheroidization occurred when the annealing temperature was increased to 900 °C.



Fig 1. SEM images of CoCrFeNiNb0.65 EHEAs in (a) as-cast state; (b) annealed at 600 °C for 24 h, (c) annealed at 750 °C for 24 h, (d) annealed at 900 °C for 24 h.

Let's break down the word EHEA and discuss about it briefly. **The word eutectic comes from the Greek words "eu," meaning "good" or "well" and "tecsis," meaning "melting".** So, we already have the idea that eutectic means a liquid converts into two or more solids if it is a binary alloy and at the same time the solid melts at a particular temperature irrespective of the individual melting temperatures of the components. To be precise the melting temperature of the alloy will be lower than either of the components. Let's see this with an example of a hypothetical binary alloy.



Fig 2. A phase diagram of a hypothetical binary alloy used to represent Eutectic temperature, composition, and point. where L represents the liquid state

3. History of HEAs

For the past five centuries, alloy design for both traditional and specialty alloys have primarily concentrated on the use of one principal element, with small inclusions of alloying elements [J.W.Yeh et al., 2014]. This alloy designing approach aided in the evolution of numerous useful alloys that benefited civilization and society. However, this restricts the configurational degree of freedom, making it difficult to develop novel alloys and applications. In the 18th century, Karl Achard (a German physicist and metallurgist) began to break through these barriers. He attempted to comprehend multi-component alloys with 5-7 elements in equi-mass compositions [Smith C.S., 1963].

He published quinary, sexinary, and septenary alloys in as-cast circumstances along with binary, ternary, and quaternary alloys, as part of his research on prospective alloys design. Achard tested these alloys for density, strength, hardness, ductility, hardness, file resistance, polishability, and finally the outcomes of exposing the polished surface to moist air, dry air, and moist air with HCl

acid fumes & moist hydrogen sulphide. He stated in his book that the properties of these new alloys differ significantly from those of pure metals and are unexpected. His is primarily made up of the consequences of these alloys, with little explanation [Achard F.C., 1788].

After a long hiatus, in 1981 the area of multi-component alloys was re-ignited by Cantor and his student [J. W. Yeh et al., 2014]. These individuals mixed several elements to create many equiatomic alloys, setting world record for making a multi-component alloy containing 20 elements, at 5 at% each. The 20-element alloy was found to be crystalline, brittle and multiphase when as-cast and also after melt spinning, but included a surprising amount of primary FCC phase. Furthermore, under non-equilibrium solidification conditions, the reported number of phases is significantly below the maximum possible. In the early 2000s, Cantor approached with the thought of equiatomic substitution as a way to investigate metallic glasses [Cantor et al., 2004].

Coincidentally, Yeh began working on multi-component alloys on his own in 1995 and later developed his notion of high mixing entropy, which he believes will help reduce the number of phases in this high order of mixing while still providing important features. Yeh studied the corrosion resistance, hardness, microstructure of fully annealed and as-cast states of 40 equiatomic alloys with 5-9 elements generated by arc melting [Yeh et al., 2004]. Ranganathan has spent a significant amount of time studying and exploring multi-component alloys. To introduce 3 new areas: high-entropy alloys, metallic glasses, superelastic and superplastic alloys, he published an article after a fruitful conversation with Yeh. It is the first open paper on High entropy alloys [Yeh., 2003].

4. Definition of HEAs

There is no general definition for high entropy alloys; each group in this field has defined them differently, which leads to confusion. A solid solution with single-phase is perhaps the most popular explanation or simplification that differs from the fundamental definitions. It is, nonetheless, considered a component of it. The most commonly used meanings are shown below.

HEAs are "made of five or more primary elements in equimolar ratios," according to an early description provided by Yeh and termed by Cantor. The equimolar concentration is limiting, and the definition continues with "principal elements with each element's concentration between 5 and 35 at%." [2004, Yeh et al.] As a result of this section of the explanation, we can conclude that the

number of possible HEAs increases even further when the concentration is in equimolar ratios. There is no mentioning of the degree of entropy, and no necessity of formation/presence of solid solution with single-phase in this composition-based formulation [Senkov O.N. et al, 2016].

Yeh provided a new concept for the configurational entropy of HEAs [Yeh ., 2006]. The idiom "high-entropy" influences the creation of a definition constructed on the magnitude of the entropy [Senkov O.N. et al , 2016]. Let us first define the term entropy before moving on to the definition. Entropy is a thermodynamic word used to calculate the amount of energy available for usable work in a thermodynamic process, such as in engines, machines or energy-conversion devices [Zhang et al., 2014]. The entropy equation is

$$dS = \frac{\Delta Q}{T}$$

where 'S' stands for entropy 'Q' for heat flow and 'T' for absolute temperature

The dimension of thermodynamic entropy is energy over temperature and the unit of Joules per Kelvin (J/K). The entropy of a system is directly connected to the logarithm of the frequency of occurrence of a microstate or the number 'W' that offers the potential microstates corresponding to the macroscopic state of the system, according to Boltzmann's theory [Gearhart 1990]. where

'k' is Boltzmann's constant = 1.381023 J/K and the logarithm is natural base "e" [Zhang et al., 2014].

The Gibb's free energy of mixing for alloy systems is expressed as

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

Where ΔG_{mix} is the Gibbs free energy of mixing,

 ΔH_{mix} is the enthalpy of mixing,

T is the absolute temperature,

and ΔS_{mix} is the entropy of mixing

According to the aforementioned equation, if ΔH_{mix} is kept constant, Gibbs free energy will be lowered and the alloy system will be more stable as a result of larger mixing entropy, [Zhang et al., 2014]. The above equation's mixing entropy contains four primary aspects that contribute to the entropy: vibrational entropy, configurational entropy, electronic randomness, and magnetic dipole, and the expression for their relationship is as follows:

$$\Delta S_{mix} = \Delta S_{vib} + \Delta S_{conf} + \Delta S_{mag} + \Delta S_{ele}$$

Configurational entropy is the most among these four entropies [Swalin R.A., and Rice R.A., 1963; Fultz 2010]. As a result, configurational entropy is widely utilized to represent mixing entropy in order to simplify complex computations and resolve residual contributions [Gao et al., 2016]. For a random solid solution having 'N' number of components, the mixing configurational entropy is given

 $\Delta S_{conf} = -R \sum c_i ln c_i$

where R is the universal gas constant = 8.31 J/K mol

and c_i represents the molar content of ith component

And the configurational entropy reaches maximum value, when the alloy is equiatomic and equimolar and the equation can be further expressed as

$$\Delta S_{conf} = R InN$$

Based on the values obtained from the above equation, we can differentiate them as low entropy, medium entropy and high entropy alloys. For high entropy, the value should be greater than 1.5R and should be <1R and >1R<1.5R for low and medium entropy alloys.



Fig 3. (A) 5 components in equiatomic ratio before mixing and (B) mixing to form a random solid solution. Assume their atomic sizes are same.

4.1 Four core effects

The characteristics and microstructures of HEAs are affected by different factors. Among them there are four major core effects. Out of these four, sluggish diffusion effect, lattice distortion

effect, and high entropy effect were proposed by Yeh [Yeh ., 2006] and the cocktail effect was proposed by Ranganathan [Ranganathan S., 2003]. The sluggish diffusion effect aids in the reduction of kinetics in microstructural processes including creep, grain growth, recrystallization. The lattice distortion effect improves the chemical and mechanical properties. The impact of high entropy causes the material to create simpler solid solution phases, which are commonly BCC and FCC. At last, the cocktail effect is believed to improve alloy's properties due to development of composite effect qualities at atomic scale [Yeh et al., 2014]. Except for the cocktail effect, all three them have been shown to have flaws.

5. Experimental results and discussions

5.1 Thermo-Calc Results

The aim of this project is to develop a eutectic multicomponent alloy, preferably FCC and BCC eutectic mixture, leading us to a better synergy between strength and ductility. With this intension being clear, we went to literature and found that there is no single rule which justified all the eutectic multicomponent alloys people have developed. Thus, we through to combinatorial mixture of a perfect FCC and a perfect BCC. After we are looking at the entire periodic table, we restricted ourselves to work with the following 13 elements, considering cost, availability, density, and manufacturability, which are, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Hf, W, Ta. As first discovered by Cantor et al., 2004 we clearly know that CoCrFeMnNi can be a good equiatomic high-entropy alloy of FCC. Noting that, the first eutectic high entropy alloy is **AlCoCrFeNi2.1**, and with increasing Co people have observed a better high temperature strength, motivating us to use Co in our system. Even though it is little costlier, when compared to other elements, literature supports Co being a high-temperature element. We understood that Co-Ni with an enthalpy of mixing -0.20 KJ/mol (Takeuchi et al., 2010) is perfect solid solution and a thermos-calc phase fraction plot revealed that it is perfect FCC and 50:50 atomic percentage.

Now it is clear that we are having an FCC/disordered FCC-L12 in our Co-Ni as per our thermocalc plot. As now there is soft phase, we need to have a hard-phase combined with it to get the strength-ductility synergy. Then we realized from the literature that, a Fe-Cr or V-Cr can be a good BCC mixture based on enthalpies of mixing -1.4/-2.0 (Takeuchi et al., 2010). We went to thermoscalc phase fraction plot and understood V-Cr is a perfect BCC at 50:50 atomic percentage. Now we combined V-Cr and Co-Ni, to get CoCrNiV but surprisingly it is not a eutectic, it is just a two-phase composition based on thermos-calc phase fraction plot. Then we systematically varied the Co-Ni w.r.t to V-Cr and realized that at (51.14CoNi-48.86VCr) is a eutectic according to pseudo-binary phase diagram. As per literature, the effect of Al in eutectic multicomponent alloys is well studied, and understood that it promotes the BCC formation by combining with Ni. Also, adding aluminum will definitely reduces the density, such that we systematically varied the content of Aluminum from 1.0 to 8 atomic percent and realized that at this particular composition 5at% we are able to get eutectic nature. This further evidenced by Scheil solidification plot which accounts for non- equilibrium solidification method.



Fig 4. Thermo-calc phase fraction plot of V-Cr at 50:50 at% with perfect BCC crystal structure



Fig 5. Thermo-calc phase fraction plot of Co-Ni at 50:50 at% with perfect FCC crystal structure



Fig 6. Thermo-calc phase fraction plot of AlCoNiVCr



Fig 7. Pseudo-binary Phase Diagram of CoNiVCr, varying Ni



Fig 8. Scheil solidification plot

The alloy $Al_5C_{24.32}Cr_{23.18}Ni_{24.32}V_{23.18}$ is prepared via vacuum arc melting. Scanning electron microscope (SEM) energy dispersive spectroscopy (EDS) of JEOL 7610-Fplus, were performed to ensure that the elemental dispersion is uniform in the lattice.

5.2 Vacuum Arc Melting of the Alloy

The alloy $Al_5Co_{24,32}Cr_{23.18}Ni_{24,32}V_{23.18}$ was prepared from pure elements (99.9% purity) through vacuum arc melting and suction casting process. Arc melting is a method of melting metals, usually to create alloys. The system is made up of three primary components: a power supply (TIG–600Amp), a chiller, and a vacuum unit. A vacuum of 10^{-6} m bar can be achieved using the vacuum

unit with rotary and diffusion pumps. An electric arc is created by a tungsten electrode striking metals in a depression (crucible) in the copper hearth. The chamber is evacuated and subsequently refilled with argon gas during vacuum arc melting. As a result, melting takes place in an argon environment. The power supply is a typical Tungsten Inert Gas (TIG) welding equipment. The heat generated by the electric arc between the electrode and the metals melts the metals in the crucible, resulting in the formation of an alloy. To improve the alloy's homogeneity, it is melted several times. A 'tweezer mechanism' can 'turn over' elemental metals after they have melted and solidified without breaking the vacuum (and then re-melted). The melt does not oxidize since the chamber is evacuated (Ar does not react with molten metal as it is an inert gas). This is the basic principle of vacuum arc melting. The metals can be heated to over 2000 degrees Celsius. The copper hearth and the electrodes are both cooled by the chiller's cold circulation water.



Fig 9 (a) Arc melting unit



(b) Suction cast sample

5.3 Metallographic polishing

To perform SEM, the sample has to be clean and mirror polished. For that the sample was sectioned perpendicular to its length using low speed diamond cutter. For polishing to be done the sample was mounted using cold setting liquid and powder. The sample was mounted as it would be easier to hold due to its small size. Cold mounting is usually performed by placing the die of the required mold size on a flat glass/table and the sample is placed in the center of the die cavity. Then the powder and liquid are mixed in the 2:1 ratio and the cavity is filled with this mixture. The mold gets cured in less than 10 minutes. Then the sample was polished until mirror finish was obtained and then cloth polished. After this, the sample was removed from the mount and cleaned with digital ultrasonic cleaner to remove the micro aluminum particles which were adsorbed during cloth polishing.



Fig 10. Mirror polished mounted sample

5.4 Differential scanning calorimetry (DSC)

DSC is a thermal analytical technique that detects physical and chemical changes within a substance as a function of temperature. The equipment offers both qualitative and quantitative data about endothermic and exothermic processes or changes in heat capacity. These processes and changes in a material are important to understand the material properties. S. Watson and M. J. O'Neill invented this technique in 1962, and it was commercialized at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

Differential scanning calorimeter at its most basic is a DSC system that subjects a small sample to variations in temperature and measures the response of that material. The sample is placed into a pan, which is then inserted into the cell of the machine. The cell is where the test is conducted and the data is collected. The DSC exports information on the temperature and heat flow through the sample to remove effects of the internals of the DSC machine. The heat flow from an empty reference pan is analyzed to the heat flow from the sample and removed. The result is information that tells you how much energy the sample has absorbed or released and how the sample has changed with respect to temperature.



Fig 11. DSC plot of Al₅C_{24.32}Cr_{23.18}Ni_{24.32}V_{23.18}

5.5 Scanning electron microscope (SEM)

The scanning electron microscopy is one of the most fascinating audit methods. The main segments of the microscope are electron beam generation column, vacuum pump, specimen chamber, monitor and control panels. The material tester turns on the vacuum pump control and vents the specimen chamber. The upper part is the so-called column it is used to generate an electron beam the lower segment consisting specimen chamber with cover plate in the longitudinal section the flange leading to the high vacuum pump is visible at the bottom thereby high vacuum is produced inside the entire microscope. The round specimen stage may not only be moved to the left and to the right but likewise in all other directions it may also be twisted and rotated.

The samples which need to be examined are placed on the specimen stage. And then V-shaped thin tungsten wire is used to create electron beam. Electric current heats the thermionic cathode, which sends electrons into the vacuum. A copper disc with a central borehole is inserted beneath the cathode. The anode is connected to the positive pole of a high voltage source, while the thermionic cathode is attached to the negative pole. For the purpose of simplicity, further necessary components have been omitted. The electrons are accelerated downward by the strong electric field between the cathode and anode. These electrons are referred to as fundamental electrons. They generate a wide divergent beam that strikes the specimens and the stage. However, the beam of primary electrons is not yet practical in this manner. Finally, the electromagnetic lens focuses

it on the specimen surface. Primary electrons wipe off electrons from the sample material at the point of incidence. Secondary electrons are electrons that have been knocked out. A raster scan generator, electromagnetic deflection, a computer with a monitor, and a secondary electron detector, abbreviated as SE detector, are also required. The scanning electron microscope's core idea is to detect secondary electrons and use them to form an image. A positively biased grid is put in front of the detector to maximize the quantity of observed electrons. The grid attracts secondary electrons and directs them to the SE detector, resulting in a magnified image of the sample. The raster scan generator focuses the electron beam to the left rear area of the sample and stops there for a short period of time, recording the quantity of secondary electrons in the SE detector. The signal is amplified and presented as a dot in the monitor's upper left corner. The electron beam pan turns slightly to the right and stops again, and the measurement is repeated. The following points on the sample are dealt with in the same manner. The premise is that numerous recorded secondary electrons lead to a bright picture point, few to a grey image point, and none to a black image point. This method covers a whole row. Then another row, until a rectangular area is scanned and an image displays on the monitor. The raster scan employs a large number of picture points rather than only a few. From fig.11 we can see clearly see that the eutectic phase was not formed. The formed phase could be FCC. From thermo-calc results it formed eutectic at 5 at% of Al but experimentally it did not form. We can try varying the Al to less than or greater than 5at% and might achieve eutectic.



Fig 12. SEM image of the sample

5.6 Vickers Hardness

The primary principle of this Vickers hardness testing method is to force a pyramid shaped diamond indenter onto the specimen with a precisely determined force and then measure the indentation's surface area. First, we have to prepare the testing machine. For that, the four-sided pyramid shaped indenter should be inserted to the mounting device of the testing machine. The specimen is then put on the support table, and the microscope lens is rotated into its working position using a hand wheel to adjust the height of the support table until the surface of the test piece appears in focus on the screen. Next, we move the test piece around on the support table until the right spot for the hardness test is displayed. Now that everything has been prepared, let's begin with the test. After pushing the start button, the diamond pyramid pans down and carefully touches the specimen surface. After maintaining a steady test force for a period of time, the test force gradually climbs to the specified value. The indenter is raised once more, and the lens of the microscope returns to its original position. This is the magnified indentation's corners.. Doing that we can easily measure the length of the two diagonals. Finally, we only have to push the input key. The Vickers hardness value will then be calculated automatically.

Vickers hardness $HV = \frac{Test force F}{Surface area of indentation A}$

The hardness was performed using Vickers Hardness Tester at a load of 4.9N with a dwell time of 20 seconds. The diagonals of the indentation are employed to measure the hardness of the sample. 30 tests were done in each sample to obtain the results.

The average hardness calculated is $647.73 \pm 55.75 \text{HV}0.5/20$

Where $647.73\pm$ 55.75 is the hardness

0.5 is the load in kgf20 is the dwell time



Fig 13. Vickers hardness indentation image

6. Conclusions

The CALPHAD predicted EHEA $Al_5(VCr)_{46.36}(CoNi)_{48.64}$ did not become eutectic experimentally. One possible explanation for this could be the Al content. We need to vary the Al content lower than 5 at% and more than 5 at% systematically to see the eutectic morphology. The DSC too is a further evidence that there is a large region of melting indicated multiple phases. When observed in SEM micrograph, we were able to guess that it is a primary FCC followed by some solid-state transformation as indicated by the continuous pores.

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