

Study on High Entropy Alloy Metals

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Abstract- *The conventional alloys like steel, super alloys, etc. are based on one principal element with alloying additions done to improve their structural and functional properties. In contrast, high ratios. They exhibit simple solid solution structures owing to their High Entropy Alloys (HEAs) are multicomponent alloys having constituents in equiatomic or near equiatomic configurational entropy. HEAs have been shown to possess good creep strength, excellent oxidation corrosion and wear resistance, high hardness, superior thermal and chemical stability and good magnetic properties. Therefore, HEAs are being explored for variety of applications and have gathered attention of scientific community worldwide. Our studies diverse aspects of high entropy alloys such as phase prediction using thermodynamic and kinetic principles, fundamental properties like diffusion, alloy coating, their applicability as high temperature coating material.*

Keywords- High Entropy Alloys, Thermodynamics and Kinetic Principles, Diffusion, thermal barrier coatings.

I. INTRODUCTION

High Entropy Alloys or HEAs[1] for short, are alloying systems composed of at least 5 elements at almost equal quantities. Rely on the maximization of Configurational Entropy, which is able to stabilize solid solution phases, against intermetallic compounds. HEAs were firstly reported in 1996 by Huang KH and Yeh JW, however the interest for the field didn't develop until 2004, when the two separate teams of Jien-Wei Yeh and Brian Cantor published some significant results. The field of High Entropy Metallurgy is still in research today as there are many phenomena not completely understood. Their multicomponent nature, raises complexity in the system and thus makes it difficult to analyze and predict their behavior.

HEAs exhibit some quite exotic effects, most of which have only been observed in High Entropy systems. These phenomena are called "Core Effects" and they originate from complex interactions among the constituent elements. The most important of them are the "High Entropy Effect", the "Sluggish Diffusion Effect", the "Severe Lattice Distortion Effect" and the "Cocktail Effect". The "High Entropy Effect" is the base on which HEAs are created. It implies that a

disordered solid solution phase can be stabilized when the entropy is sufficiently high. HEAs have extremely increased entropy as they are near equimolar. The "Sluggish Diffusion Effect" proposes that kinetics transformations in HEAs are very slow in comparison to conventional alloys. This is partly because of the increased activation energy for substitutional diffusion and partly due to local atomistic phenomena that eventually stall diffusion. Furthermore, the "Severe Lattice Distortion Effect" suggests that the crystalline structure of HEAs is extremely deformed. Although disordered solid solution phases resemble common BCC, FCC or HCP structures, are altered significantly, due to the different size among constituent atoms. Finally the "Cocktail Effect" in fers that the strength of a high entropy solid solution is much higher than simply the weighted average of the composing element strength. The addition of low strength and density alloying elements like Al, can actually make the system more resilient. Again this effect originate from complex atomic interactions.

"Core Effects" endow HEAs with extraordinary proper ties, very useful in various applications. In general single phase FCC systems tend to be very ductile, whereas single phase BCCs exhibit increased yield strength due to a pronounced solid solution strengthening. A mixture of FCC and BCC phases takes advantage of both properties, resulting in a high strength ductile material. Precipitation of sigma phase can further increase the yield stress, however it greatly diminishes ductility. For example, AlCoCrFeNiTi_{0.5} has been reported to have a yield strength of 2.26 GPa and a plasticity of 23%. Furthermore, many HEAs perform exceptionally well at elevated temperatures as a result of the decreased kinetics. They have excellent creep behavior as they are very stable and resist thermal softening, even at very high temperatures addition, due to their low diffusivity HEAs have found implementation as diffusion barrier coatings. Recent studies have also shown that several HEAs are able to withstand a range of highly corrosive environments even at elevated temperatures. It should be noted that although their remarkable properties, HEAs have not yet found widespread application other than as protective coatings and high temperature components. The main reason for that is the increased cost associated with the material and the large scale manufacturing.

II. KEY CONCEPTS IN HEAS

A. Standard and Operational HEA Definitions

The standard definition of an HEA is an alloy that contains at least five major metallic elements ($N \geq 5$), each with concentration between 5–35 atom percent [3,5]. The idea behind this definition is that compositional complexity may not necessarily lead to microstructural complexity (*i.e.*, compound formation) due to the influence of entropy. Specifically, it is suggested that disordered solid solutions might remain stable relative to ordered intermetallic compounds (for simplicity, the terms ordered, intermetallic and compound are used interchangeably in this paper) in alloys with high total entropies of mixing (ΔS_{mix}). Whether or not an alloy satisfies the standard definition is clear based on alloy composition alone, regardless of the magnitude of ΔS_{mix} . However, since the motivation for studying HEAs often includes the magnitude of an alloy's entropy and its ability to remain a single-phase solid solution at room temperature, some discussion of these two features is necessary. How high is high? Is an alloy an HEA if more than a single disordered phase occurs in the microstructure?

Configurational entropy (ΔS_{conf}) forms a major part of ΔS_{mix} and for ideal and regular solutions is:

$$\Delta S_{\text{conf}} = -R \sum_i X_i \ln(X_i)$$

where X_i is the atom fraction of element i and $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ is the gas constant. This is a good approximation for liquid alloys and for many solid alloys near the melting temperature. A maximum ΔS_{conf} occurs in equimolar alloys, where the atom fraction of all elements is $X_i = 1/N$, so that $\Delta S_{\text{conf}} = R \ln(N)$. HEAs thus favor equimolar compositions, but are not limited to them as stated in the HEA definition above. In equimolar HEAs, ΔS_{conf} ranges from $1.61R$ for $N = 5$ to $2.57R$ for $N = 13$ [5]. ΔS_{conf} varies in a system of a given N by deviating from equimolar concentrations within the bounds of the HEA definition. A lower limit of $\Delta S_{\text{conf}} = 1.36R$ occurs for an HEA with $N = 5$ and $X_A = X_B = 0.35$, $X_C = 0.20$ and $X_D = X_E = 0.05$. This value can be compared with $\Delta S_{\text{conf}} = 1.39R$ for equimolar 4-component alloys. Conventional alloys have S_{conf} that range from about $0.22R$ for low alloy steels to about $1.15R$ for stainless steels [5]. Super alloys (so-named either because of their exceptional balance of properties or by the fact that they contain as many as 12 alloying elements) have configurational entropies as high as $1.37R$ [5]. There is no

single ΔS_{conf} value agreed upon in the HEA community for specifying HEAs. The lower limit of $1.36R$ gives some ambiguity, since an equimolar 4-element alloy has a higher $\Delta S_{\text{conf}} = 1.39R$ but is excluded by the standard HEA definition. Further, the lower limit of $1.36R$ overlaps with

conventional alloys, raising the question of the uniqueness of HEAs. In the present paper, we consider any alloy with $\Delta S_{\text{conf}} \geq 1.5R$ as an operational definition of an HEA. This is nearly in the middle of the ΔS_{conf} range for $N = 5$ HEAs. This excludes a small number of compositions allowed by the standard definition, but has the advantages of being clearly higher than conventional alloys and excluding 4-component equimolar alloys. It is also consistent with an earlier ranking: low entropy alloys have $\Delta S_{\text{conf}} < R$; those with $R \leq \Delta S_{\text{conf}} \leq 1.5R$ are medium entropy alloys; and those with $\Delta S_{\text{conf}} \geq 1.5R$ are HEAs [5]. This gives S_{conf} that is at least 50% higher than S_{fusion} of pure metals (see Richards' Rule, [6]). Comparing to the Dulong-Petit Law and equi-partition theorem [7], this definition gives $\Delta S_{\text{conf}} \geq C_v/2$, where C_v is the molar heat capacity. Another debate within the HEA community is whether or not an alloy with more than one phase is an HEA. Consider two 5-component equimolar HEAs that are both solid solutions near their melting points. The first, HEA-1, remains a single-phase solution at 300 K while the second, HEA-2, forms a binary compound at a temperature (T_{rxn}) that removes two elements entirely from the solid solution (Figure 1). Both alloys have $\Delta S_{\text{conf}} = 1.61R$ at high temperature, but ΔS_{conf} of the disordered phase is reduced to $1.10R$ in HEA-2 below T_{rxn} . Since HEA-2 has two ΔS_{conf} values, we must consider which is used in defining whether or not it is an HEA. It has been suggested that ΔS_{conf} of the low temperature state be used [8]. We suggest the alternate approach, since judging the entropy available to a system by its final (low temperature) state is like judging the strength of an athlete at the end of a race, after all energy has been spent. We discard useful information concerning the athlete's overall strength and competitiveness and judge the athlete only on whether the current race was won or lost. Phase stability is a competition between entropy, enthalpy and other terms such as strain energy that are summed in the Gibbs free energy equation. The entropic energy ($-T\Delta S_{\text{conf}}$) becomes less negative with decreasing temperature, and so phases with enthalpies of formation (ΔH_f) sufficiently large and negative to overcome $-T\Delta S_{\text{conf}}$ at lower temperature may form in HEAs. These could be called high enthalpy alloys since both ΔS_{conf} and $|\Delta H_f|$ are large, but in the present work these are still considered HEAs as discussed below.

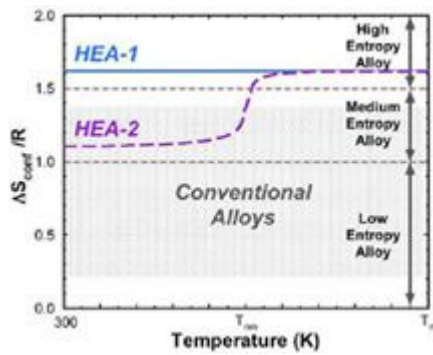


Figure 1. $\Delta S_{conf}/R$ v temperature for two equimolar 5-component alloys.

Figure 1 illustrate entropy differences between high and low temperature states. HEA-1 is a single-phase solid solution over the full temperature range and a binary compound forms in HEA-2 at T_{rxn} . HEAs are defined here by the magnitude of ΔS_{conf} in the high temperature state.

B. Composition of High Entropy Alloys

High Entropy Alloys (HEA) are made of many metals mixed in desired Proportions. Usually the HEA’s are made of

Al, Fe, Co, Ni, Cr, Mg, Zn, K, and Cu i.e.

- AlFeCoNiCr,
- CaMgZn,
- AlFeCoCrNiCu,
- FeCoNiCrCu,
- FeCrNiAlLa, etc.,

C. Methods of preparation of HEA’s

High entropy alloys are made[2] by several methods. They can be prepared in vacuum arc induction melting furnace, equivalent thermal entropy method, powder metallurgy method, and simple casting method.

Some of the Preparation methods and properties of high entropy alloys are given below.

Table 1. Preparation methods and properties of high entropy alloys

HEA	Preparation method/Properties	Method and Spectroscopy	Finding/Application
Al _x FeCoNiCr(B)	High entropy alloys were prepared in a vacuum arc in-duction melting furnace.	Electrochemical investigation	The microstructure is a simple solid solution structure, and the fraction of FCC crystal structure decreased with increasing of Al content. Chromium tends to segregate at the inter-dendrite grain boundary
Ca ₆₅ Mg ₁₅ Zn ₂₀	A Ca ₂₀ Mg ₂₀ Zn ₂₀ Sr ₂₀ Yb ₂₀ high-entropy bulk metallic glass was fabricated with unique properties of high-entropy alloys.	In vitro tests, in vivo animal test	The mechanical properties and corrosion behavior were enhanced. The in vitro tests showed that the Ca ₂₀ Mg ₂₀ Zn ₂₀ Sr ₂₀ Yb ₂₀ high-entropy bulk metallic glass could stimulate the proliferation and differentiation of cultured osteoblasts. The in vivo animal tests showed that this high-entropy bulk metallic glass did not show any obvious degradation after 4 weeks of implantation, and they can promote osteogenesis and new bone formation after 2 weeks of implantation.
Al _x FeCoCrNiCu (x=0.25, 0.5, 1)	HEA is gradually changed from a single FCC to FCC phase and BCC phase with the addition of Al. With the addition of Al from x=0.25 to 1.0, the hardness of the alloys increase from 165 to 485 HV correspondingly addition of Al. With	Polarization curves	The polarization curves show that alloys has the better corrosion resistance than 304 stainless steel in 0.5 mol L ⁻¹ H ₂ SO ₄ solution and 1mol L ⁻¹ NaCl solution, and meanwhile Al _{0.5} FeCoCrNiCu high-entropy alloy has the best comprehensive

	the addition of Al from $x=0.25$ to 1.0, the hardness of the alloys increase from 165 to 485 HV correspondingly		corrosion resistance.
K4169	The Cell Automaton technology was adopted to couple simulate the grain structure formation process of K4169 superalloy blade with its temperature fields using continuous nucleation model and kinetic model of dendrite tip growth	Equivalent thermal entropy method	In order to control the grain structure of K4169 superalloy blade which affects its mechanical performance and ability of resistance to corroding in high temperature state, the transient temperature field distributions were analyzed. The relationships between temperature and time of every point on vertical section and cross section during phase change heat transference process of K4169 superalloy were obtained.
CrFeNiCuMoCo	Powder metallurgy method.	SEM/EDS, XRD micro-Vickers hardness test, electro-chemical methods	The morphology of the CrFeNiCuMoCo HEA is simple, the phase mainly composes of FCC and BCC; Mo and Cu are segregated in the alloy; the alloy shows excellent corrosion resistance, the corrosion current density decreases by an order of magnitude compared with 304 stainless steel.
AlCoCrFeNiTi 0.5	The AlCoCrFeNiTi 0.5 high-entropy alloys fabricated by cold crucible levitation melting (CCLM)	Electrochemical methods	The alloy exhibits a superior resistance to tempering and softening property. The tempering treatment improves corrosion properties in a 3.5 % NaCl solution, and the alloy tempered at 700 °C exhibits the best corrosion property among the experimental alloys.

D. Properties of High Entropy Alloys

High entropy alloys have unique properties and applications. $\text{Ca}_{20}\text{Mg}_{20}\text{Zn}_{20}\text{Sr}_{20}\text{Yb}_{20}$ has biomedical application. It promotes bone formation.

HEA's have high corrosion resistance. For example $\text{Al}_{0.5}\text{FeCoCrNiCu}$ has high corrosion resistance. Its resistance is better than that of 304 stainless steel in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and $1 \text{ mol L}^{-1} \text{ NaCl}$ solution. Corrosion resistance of CrFeNiCuMoCo increases and its corrosion current density decreases. AlCoCrFeNiTi0.5 alloy has good corrosion resistance in 3.5 % NaCl solution. Tempering treatment of this alloy improves its corrosion resistance. Iron alloys have high strength and ductility. They have high resistance to oxidation and corrosion. They can be considered for structural metallic materials.

The properties of high entropy alloys have been investigated by various techniques such as polarization study and AC impedance spectra.

The surface morphology has been analyzed by methods such as SEM, EDS, X-rays diffraction, selected area diffraction and differential scanning calorimetry. The surface of high entropy alloys has fcc phase and bcc phase. Addition

of one element to the *mixture* sometimes changes the phase. For examples when Al is added the phase of AlFeCoNiCrTi alloy changes from fcc to bcc phase.

The composition of high entropy alloys, the methods of preparation of alloys, their properties, uses, methods of studying the HEA's, and the surface morphology of HEA's are summarised in Table 1.

III. PHASE PREDICATION PRINCIPLES

A. Thermodynamic Phase Predictions In High Entropy Alloys

Thermodynamics phase predication[3] of HEAs by using the CALPHAD (CALculation of PHase Diagram) technique. The challenge in applying this technique for HEAs

is in developing a Gibbs energy database that works for wider range of compositions. This technique uses extrapolation of thermo chemical data of lower order systems (binary and ternary) to higher order systems (quaternary, quinary, sexinary, etc.).

For example, phase prediction for Co-Cr-Fe-Ni alloy was done.

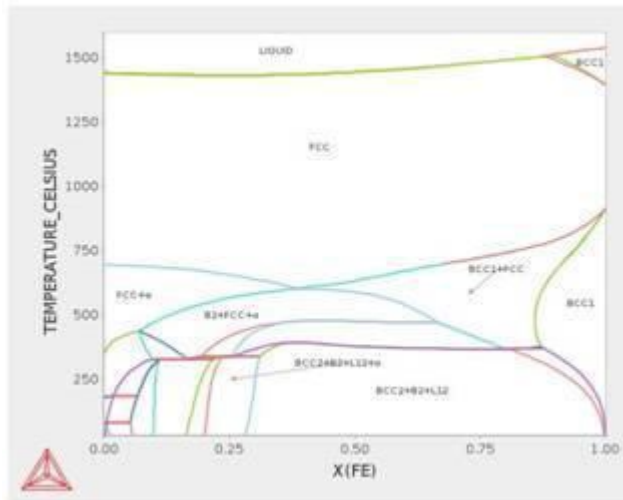


Fig 1. Isolethal section of Co-Cr-Fe-Ni system

Using such Gibbs energy database in combination with Thermo-Calc software. Fig. 1 shows a isoplethal section in Co-Cr-Fe-Ni phase diagram. Fig. 2 shows the phase fraction plot for the equiatomic CoCrFeNi alloy

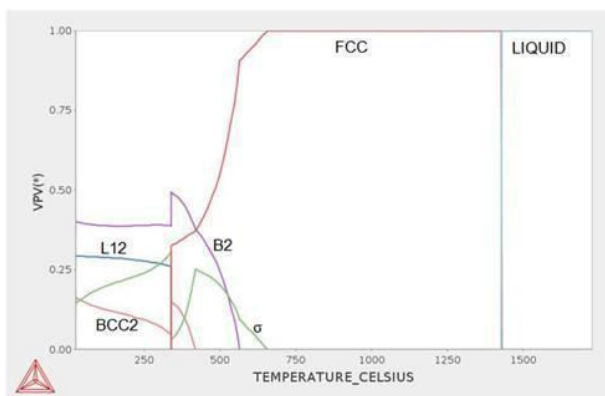


Fig 2. Phase fraction plot for equiatomic CoCrFeNi alloy

For validation of these predictions, alloys are prepared by vacuum arc melting. In order to achieve the equilibrium microstructure, long term heat treatments are being done at various temperatures.

B. Kinetic phase predictions in High entropy alloys

Phase prediction in high entropy alloys (HEA) is a prime challenge for materials engineers[5] as the final phase determines the properties of the HEA. Several approaches depending on thermodynamic, topological or electronic properties of constituent elements have been explored so far without much success. Moreover, most importantly, the formation of phase has been observed to be greatly dependent on processing route. For ex. an alloy may form BCC by Cu-mold casting, however, it can result in amorphous phase formation by melt spinning. The kinetic dependence of phase transformation which basically predicts the phase formation at different cooling rates has not been studied so far for HEAs. A simple and completely predictive approach has been explored to predict whether an equiatomic combination of elements will form amorphous, BCC, FCC or HCP single phase or a combination of two/three of these or the combination with the presence of one or more intermetallic compounds (IM). This approach is based on the variation of viscosity of alloys or IMs as a function of temperature utilizing the viscosities of its constituting elements and suitably incorporating the crystal structure information. Some other parameters affecting viscosity of an alloy like atomic size, packing density of the unit cell, etc., are suitably incorporated in the model. The TTT diagrams for each probable phase are generated with the help of the viscosity data. The formation of the amorphous, BCC, FCC single phase in HEAs has been excellently predicted by this approach with utmost success. The most important part of the present approach is that it acts as an efficient guide about the processing route that should be adopted to form a particular phase or combination of phases with or without IMs in a particular alloy via the critical cooling rate R_c obtained through the predicted TTT diagrams.

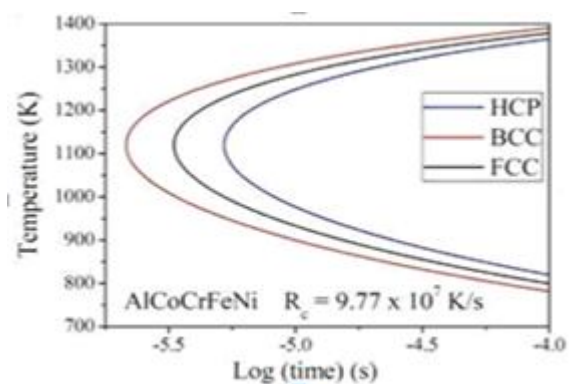


Fig 3.a. Structure of AlCoCrFeNi

Fig 3.a. shows that the BCC phase is the most stable one in AlCoCrFeNi HEA followed by FCC. The amorphisation would happen at a cooling rate of nearly 10^8 K/s. Therefore, it is predicted that, even melt spinning with 10^6 K/s cooling rate cannot vitrify the alloy.

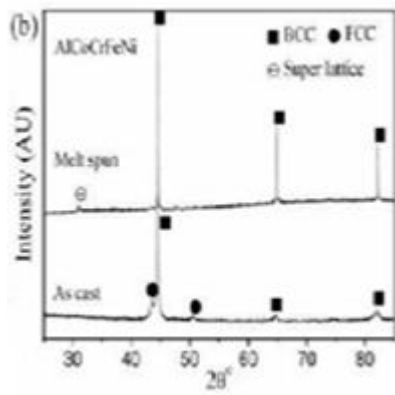


Fig.3.b. The XRD results of arc melted AlCoCrFeNi

The Fig.3.b. shows the XRD results of arc melted AlCoCrFeNi sample having BCC phase with a minor presence of FCC whereas, the melt spinning results in BCC phase formation and not amorphisation, validating the model.

C. Diffusion in High entropy alloys

Sluggish diffusion[5] has been put forward as one of the core effects in high entropy alloys (HEAs) and is believed to be responsible for their high thermal stability and creep resistance. Slower diffusion is also presumed to play a role in phase evolution and promote formation of nano-precipitates and amorphous phases in many HEAs. However, till date, reports on diffusion in HEAs are scarce and it has only been measured using inter diffusion approach.

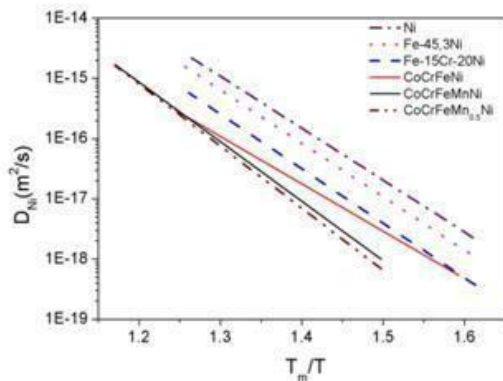


Fig.4. Ni tracer diffusion coefficients in high entropy alloys and other FCC systems (CoCrFeNi & CoCrFeMnNi [1], Ni [2], Fe45.3Ni [3], Fe-15Cr-20Ni [4], CoCrFeMn0.5Ni [5])

Fig.4 .shows the Ni tracer diffusion coefficients measured for CoCrFeNi and CoCrFeMnNi, and comparison with other FCC systems [1]. It is clear that diffusion rates slow down with the increase in number of components.

D. High Entropy Alloy Coatings.

HEA composition that can be a possible alternative to present day bond coats used in thermal barrier coatings[6]. Traditionally, TBCs are thermally insulating ceramics bonded onto superalloy components via metallic bond coats, which are usually Ni based dual phase alloys having sufficient Al to form an oxidation resistant alumina layer during service.

However, over time this oxide layer thickens and spalls off under thermal cycling strains, thereby compromising the entire TBC. At the same time, diffusion of rare earth elements from the bond coat into the superalloy is another serious issue that deteriorates the mechanical properties of the component. HEAs can thus be possible candidates for bond coats, owing to sluggish diffusion through them.

A slow growing yet resilient oxide layer, or possibly a high entropy oxide layer can provide the desired protection from oxygen ingress. Towards this, we are looking at alloy compositions based on Al, Ni, Co, Cr, Ti, Fe with minor additions of reactive elements such as Y, Zr, Yb, etc.

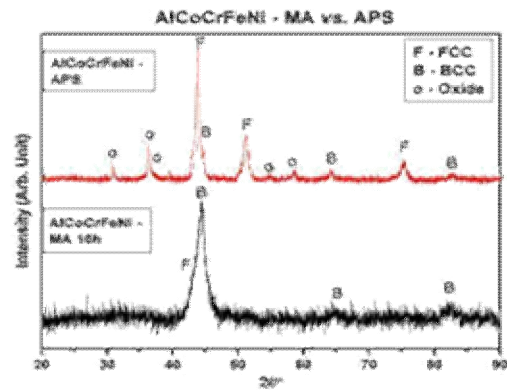


Fig.5. XRD patters of mechanically alloyed AlCoCrFeNi powder vs. APS coated AlCoCrFeNi

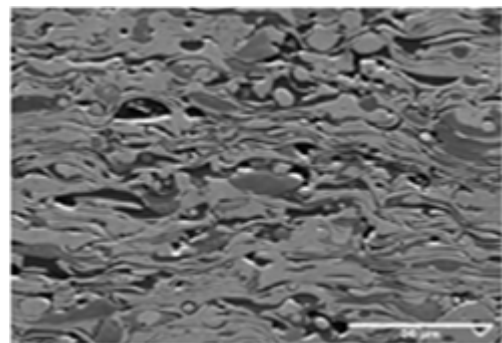


Fig.6. BSE image of APS coating cross section. Dark grey phases are oxides, while light grey ones are metallic phases. Powders are synthesized by mechanical alloying, done here at IITM, and are coated via (i) Atmospheric Plasma Spray(APS) at Swinburne University of Technology with Prof. C.C. Berndt, and (ii) Cold Spray, done at ARCI, Hyderabad.

APS results in a composite microstructure, with alumina and Al-Cr rich oxides interlaced with metallic splats, whereas Cold Spray does not see any oxidation or melting of feedstock. The plasma sprayed coatings showed a hardness of about 4GPa while the conventional NiCrAlY coatings usually give a hardness of about 2.5GPa.

IV. CONCLUSION

In this paper, we gave a strategy to explore, evaluate and develop high-entropy alloys (HEAs) for structural applications in the transportation and energy fields. The main ideas are summarized below.

“High-Entropy Alloys (HEA’s)” has become an emerging field through the collective efforts of many researches since 1995. High mixing entropy can enhance the formulation of solution type phases for alloys, ceramics and composites, and in general leads to simpler microstructure. In this field, large degrees of freedom in composition design as well as suitable process design could provide a wide range of microstructure and properties for applications. There are many opportunities for HEMs to overcome the bottlenecks of conventional materials. In this presentation, several breakthrough applications are pointed out and emphasized. They include aerospace turbines and nozzles, car turbochargers, molds and dies, cutting tools, hard facings, radiation-damage resistant materials, cryogenic piping and containers, and low TCR materials.

V. ACKNOWLEDGEMENT

I interest in the material science and Engineering that way join with colleague Mr. K.Siva Kumar, Assistant Professor study on the High Entropy alloy materials which is advanced topic in materials science present going research on international level.

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REFERENCES

- [1] Ioannis S.Aristeidakis, Maria- Ioanna T.Tzini, Laboratory of Materials, Department of Mechanical Engineering, University of Thessaly.
- [2] Damiel B. Mivacle, Exploration and development of High Entropy Alloys for structural Applications, Entropy 2014, pp.494-525
- [3] Guruvidyathri, thermodynamic phase predication in High Entropy Alloys, International Workshop on High Entropy Materials (IWHEM-2017).
- [4] Chinmoy Chattopadhyay, National Institute of Foundry & Forge Technology (NIFFT), Kinetic approach for phase predictions in High Entropy Alloys, Internal workshop on High entropy alloys IWHEM-2017.
- [5] Mayur Vaidya, Diffusion in High entropy alloy, IIT, Chennai.
- [6] Ang, Andrew & Berndt, Plasma-Sprayed High Entropy Alloys: Microstructure and Properties of AlCoCrFeNi and MnCoCrFeNi. Metallurgical and Materials Transactions, International Workshop in High entropy alloys IWHEM-2017.