HIGH-ENTROPY ALLOYS, A REVIEW

Sumit Kumar [1], Sujit Kumar [2], Vikash Singh [3], J. Jagadesh Kumar [4]
[1, 2, 3] *Undergraduate Student, Mechanical Engineering Department, Vidya Jyothi Institute of Technology, Hyderabad, India*
[4] *Associate Professor, Mechanical Engineering Department, Vidya Jyothi Institute of Technology, Hyderabad, India*

***

Abstract - *Alloys are typically composed of one primary element, with only minor additions of other elements to modify the properties. High-entropy alloys (HEAs) are alloys with five or more principal elements. Due to the different design concept, these alloys often exhibit different and rare properties when compared to normal alloys. Thus, there has been significant focus in these materials, leading to an evolving yet exhilarating new field. The current paper briefly reviews some critical aspects of HEAs, including evolution, mechanical properties, high-temperature properties, structural stabilities, and corrosion behaviours. Current challenges and imperative future directions are also pointed out. The current and prospective applications of HEAs are also discussed.*

Key Words: High Entropy Alloy (HEA), alloy, corrosion, mechanical properties.

1. INTRODUCTION

Alloys are basically composed of one principal element, with only minor additions of other elements to modify the properties. High-entropy alloys (HEAs) are alloys constituted with equal or nearly equal quantities of five or more metals. HEAs are currently the focus of momentous attention in metallurgy and material science because they have potentially desirable properties. Five or more metals in nearly equal proportions are melted together to obtain stable random solid solutions to produce a High Entropy Alloy. High mixing entropy can enhance the formation of solution-type phases, and in general leads to simpler microstructure. The name derives by the observation that their exceptionally high mixing entropy favours stability, which means the capability to keep their microstructures fixed, without separating in different phases by ordering or segregation, as in the case of traditional alloys. Components displaying high oxidation and corrosion resistance at extreme temperatures are required for electrical, magnetic and high-temperature applications. The striking difference from traditional alloys is therefore the use of multi-components for building these new materials. Current HEA studies favour single-phase, disordered solid solution alloys. It is believed that strengthening by solid solution is more effective in HEAs than in conventional alloys. Many HEA microstructures have been produced, including single phase, multiple phase, nano-crystalline and even amorphous alloys [1].

2. EVOLUTION OF HIGH-ENTROPY ALLOYS

HEAs where 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 behaviour [1].

3. SELECTION OF CONSTITUENT ELEMENTS IN HIGH ENTROPY ALLOYS

Elements that can be used in High entropy alloys are shown below in Table 1 [2]. The main constituents of HEAs comprise metallic elements can be selected form metallic group and non-metallic elements which include C, B, Si, P, S H.

Table -1: Major constituent elements for possible use in HEAs

MAJOR METALLIC ELEMENT	MINOR METALLIC ELEMENT	MAJOR NON-METALIC ELEMENT
Li, Be, Mg, Al, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Sm, Eu, Au, Gd, Tb, Rh, Pb, Pd, Ag, Hf, Ta, W, pt, Nd,	Li, Be, Mg, Al, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sy, Cd, In, Sn, Sb, Y, Zr < Nb, Mo, Ru, Rh, Pb, Bi, Pd, Ag, Hf, Ta, W, Pt, Au, La, Ce, Ce, Pr, Nd, Sm, Eu, Gd, Tb	C, B, Si, P, S, O, N

Jien-Wei et. al proved that an arbitrary choice of a group of 13 mutually miscible metallic elements enables the design of 7099 HE alloy systems with 5 to 13 elements in equimolar ratios, citing an example of CuCoNi-CrAlFe [2].Thus, countless alloys can be produced even with elements that cannot produce chemical immiscibility. Cantor demonstrated number of alloys that have been studied which include all unitary, most binary, and a few ternary and other alloy systems. Elements for alloying are selected as follows:

- Identify all metals for structural metals from literature and standards. Starting from the periodic table elements, remove all non-metals.
- Identify desired attributes
- Use Hume – Rothery rules to find atoms within 8% of atomic size difference. This is important for cast alloys.

The properties of constituent alloying elements need to be similar: they shall have similar atomic size and similar electronegativity. However, the Hume-Rothery rule is apparently not applicable to the solid solution formation in HEAs. For example, it cannot explain why the equi-atomic

Co(HCP)-Cr(BCC)-Cu(FCC)-Fe(bcc)-Ni(FCC) alloy forms an FCC-typed solid solution, and how the addition of FCC-Al can eventually change the FCC-type CoCrCuFeNi to a BCC structure. If the effects of other minor constituents can be neglected, these compositions of different phases in multi-phase HEAs are far away from the solute composition regions where the solid solutions can be formed according to corresponding binary and ternary phase diagrams. Therefore, the thermodynamic instability provides the driving force for the precipitation under ion irradiation, which is similar with the precipitation behaviour of many immiscible binary systems.

4. PROPERTIES OF HIGH ENTROPY ALLOYS

4.1. MECHANICAL PROPERTIES

Because of the wide composition range and the enormous number of alloy systems in HEAs, the mechanical properties of HEA can vary significantly. In terms of hardness/strength, the most critical factors are:

a. Hardness/strength of each composing phase in the alloy.
b. Relative volume ratio of each composing phase.
c. Morphology/distribution of the composing phases.

The first factor is largely determined by the crystal structure and bonding of each phase. The general rule to estimate the hardness/strength of an HEA is straight forward: the harder the phase (and the higher the fraction of the hard phase), the harder the alloy. When two HEAs have phases with similar hardness and relative fraction, the distribution of the phases can also play an important role. The ductility of HEA is also related to the phase in the alloy. As can be expected, harder phases usually have lower ductility. The deformation microstructure and mechanism in most HEAs is unclear [3].

Some researchers developed HEAs that are based on totally different elements. The plastic fracture strain is less than 5% for many alloys. However, some alloys can be compressed to 50% without fracture. It was suggested that the high plasticity in some alloys is owing to the prevalence of deformation twinning [3]. It is worth mentioning that refractory HEAs can show superb mechanical properties at elevated temperatures.

Wear properties of HEAs, under both abrasive and adhesive conditions, have been tested in a number of systems. HEAs composed solely of SDPs typically do not show better wear properties than conventional alloys with similar hardness (e.g. compare Al0.5CoCrCuFeNi and 316SS). Wear resistance is clearly enhanced in the presence of some B2 or COPs (e.g. Al2CoCrCuFeNi and AlCoCrFe1.5Mo0.5Ni). If COPs with high hardness become the main phase, wear resistance is often outstanding [3].

4.2. MAGNETIC PROPERTIES

Studies regarding the magnetic properties of HEAs are mainly focused in alloys derived from Al–Co–Cr–Cu–Fe–Ni–Ti. These alloys usually contain more than 50 at % of magnetic elements (Fe, Co, and Ni). They are either paramagnetic or ferromagnetic with a saturation magnetization (Ms) typically around 10–50 emu/g (if converted by weighted average density, roughly in the range of 70–350 emu/cc). Ms of the alloy depends mainly on the composition and crystal structure. In general, more magnetic elements lead to higher magnetization. However, alloying elements can have considerable impact. The former has a high Ms of 1,047emu/cc, but addition of 25% Cr renders the alloy (CoCrFeNi) paramagnetic. A higher degree of decomposition leads to higher saturation magnetisation, coercivity and remanance. The fact that separation of Cr from Fe and Co leads to higher magnetization seems to agree with the conclusion drawn by Zhang et al., i.e., that existence of Cr leads to cancellation of magnetization. Density functional theory technique was used to calculate the atomic magnetic moment of possible zinc blende structures. Among the possible structures, Ti4(Ni4Fe4)Sn4 is magnetic and the ratio between the elements also agrees with the results of EDS analysis.

4.3. ELECTRICAL PROPERTIES

As-cast high entropy alloy typically have electrical resistivities between 100 and 220 μΩ-cm. These values are 1–2 orders of magnitude higher than that of many conventional metals, and are similar to that of bulk metallic glasses (BMG). The higher electrical resistivity of HEA originates from its highly distorted lattice that scatters electron waves. The change of resistivity as a function of temperature was studied in AlxCoCrFeNi alloys. Like conventional alloys, the resistivity of AlxCoCrFeNi increases with temperature. However, the slope of the temperature-resistivity curve the temperature coefficient of resistivity (TCR) is generally one order of magnitude smaller than that of conventional alloys. Some alloys, such as Al2.08CoCrFeNi, have extremely small TCR. The average TCR of Al2.08CoCrFeNi from 4.2 to 360 K is only 72 ppm/K, compared with several thousand ppm/K for most pure metals. The low TCR value spanning such wide temperature range enables it to be used as precision resistors in special applications [4].

4.4. THERMAL PROPERTIES

Thermal conductivity/diffusivity has been measured in AlXCoCrFeNi and AlXCrFe1.5MnNi0.5 Moy alloys. Thermal conductivity of AlXCoCrFeNi alloys falls in the range of 10–27 W/mK. These values are lower than those of most pure metals, but are similar to those of heavily alloyed conventional metals such as high-alloy steel or Ni-based super alloys. The lower thermal conductivity in HEA should be a result of its distorted lattice, which scatters the phonons more significantly [4]. Between 27 °C and 300 °C, thermal conductivity/diffusivity of these HEAs increases with increasing temperature. The enhanced heat transfer at higher temperatures in the AlXCoCrFeNi alloys was explained by the increased phonon mean free path at higher temperature, owing to thermal expansion of the lattice. Note that the electrical conductivity in the AlXCoCrFeNi alloys decreases with increasing temperature, which means that the electrical and thermal conductivities in the AlXCoCrFeNi alloys show opposite trends with respect to temperature. Therefore, the Wiedemann-Franz law is not obeyed in these HEAs.

5. BENEFITS OF HIGH-ENTROPY ALLOYS

A major benefit of HEAs is that they stimulate the study of compositionally complex alloys not previously considered. Another major benefit is that HEAs provide a way to design and produce a vast number of new alloys. Just by playing with possible combinations, each with at least five metal elements as components, a huge number of compositions becomes available. Most of them have great probability to bring about useful alloys, giving substantial potential for discoveries of important scientific and practical benefit. Even by limiting the number of new alloys to study, only to those made with completely miscible metals; it has been proved nevertheless that enormous numbers of systems are possible, wherefrom only the most useful will be pursued [5].

6. NEED FOR NEWER ALLOYS IN INDUSTRY

There still remains a great need for an improvement in the materials used in a number of applications, such as [6]:

a. Engine materials: better elevated-temperature strength, oxidation resistance, and hot corrosion (sulfidation) resistance.
b. Nuclear materials: better elevated-temperature strength and low neutron absorption.
c. Tool materials: better elevated-temperature strength, wear resistance, impact strength, low friction, corrosion resistance, oxidation resistance, and anti-sticky.
d. Waste incinerator: better elevated-temperature strength, wear resistance, corrosion resistance, and oxidation resistance.
e. Refractory building frame: better elevated-temperature strength to sustain edduring firing.
f. Light transportation materials: better strength, toughness, creep resistance, and workability.
g. High-frequency communication materials: high electrical resistance and magnetic permeability above 3 GHz.
h. Functional coatings: better wear resistance, anti-sticky, anti-finger print, anti-bacterial, and aesthetics.
i. Hydrogen storage materials for mobiles: low cost, high reversible volumetric and gravimetric density of hydrogen, and near-ambient cycling condition.
j. Superconductor: higher critical temperature and critical current.
k. Thermoelectric materials: higher thermoelectric figure of merit.
l. Golf club head: higher strength and resilience.

High Entropy alloys seem to promising to cater the above industry requirement and hence are the area of current day research.

7. FUTURE SCOPE FOR HIGH-ENTROPY ALLOYS

Due to low density and high strength, HEAs find application in transportation and energy industries. These applications require performance, reliability and endurance in extreme operating conditions [7].HEAs are good candidates to replace steel and Titanium alloys. Other applications include the compressor blades of an aero-engine which are often manufactured using Ti base alloys. Hardfacing technology can be employed whereby the HEAs are fabricated into rods and powders and then plasma arc or thermally-sprayed onto the surface of tools and other components [8]. The hardfacing process involves adding a thick layer of wear and/or corrosion resistant material by welding, thermal spray welding. Common industrial uses include moulds, dies, tools and nozzles [9]. They can be used to suppress electromagnetic interference especially in electronics. For example, at 13000MHz a coating of 1μm can be effective as a screen in commercial applications. HEAs can be used in coatings used in food preservation and cookware due to anti-corrosion, anti-oxidation and wear resistance properties. Bacteria, for example E-coli can be prevented from reproducing and building colonies. Thus there is wider scope for the application of high entropy alloys.

CONCLUSIONS

Invention of High Entropy Alloys opened new avenues in the field of metallurgy and material science. These alloys have unique characteristics and excellent properties when compared to conventional alloys. HEAs can replace many costly alloys used currently in manufacturing industry. There is a large scope of further research in HEAs which can give birth to new alloys.

ACKNOWLEDGEMENT

The authors express their deep sense of gratitude to Head of the Mechanical Engineering Department, Director and Correspondent of Vidya Jyothi Institute of Technology, Aziz Nagar, Hyderabad, for the encouragement and support extended towards the current work.

REFERENCES

[1] B. S. Murty, J. W. Yeh, and S. Ranganathan, “High Entropy Alloys,” High Entropy Alloy., no. January, pp. 159–169, 2014.

[2] S. Chikumba and V. V. Rao, “High Entropy Alloys: Development and Applications,” 7th Int. Conf. Latest Trends Eng. Technol. Nov. 26-27, 2015 Irene, Pretoria (South Africa), pp. 1–5, 2015.

[3] M. H. Tsai and J.-W. Yeh, “High-Entropy Alloys: A Critical Review,” Mater. Res. Lett., vol. 2, no. 3, pp. 107–123, 2014.

[4] M. H. Tsai, "Physical properties of high entropy alloys," Entropy, vol. 15, no. 12, pp. 5338–5345, 2013.

[5] D. B. Miracle, J. D. Miller, O. N. Senkov, C. Woodward, M. D. Uchic, and J. Tiley, "Exploration and development of high entropy alloys for structural applications," Entropy, vol. 16, no. 1, pp. 494–525, 2014.

[6] J. W. Yeh, "Recent progress in high-entropy alloys," Ann. Chim. Sci. des Mater., vol. 31, no. 6, pp. 633–648, 2006.

[7] Y. Jien-Wei, C. Swe-Kai, L. Su-Jien and G. Jon-Yiew, Nanostructured High Entropy Alloys with multiple principal elements: Novel alloy design, concepts and outcomes, Advanced Engineering Materials, vol. 6, no. 5.

[8] M. E. Glicksman, Principles of Solidification: An Introduction to Modern Casting and Crystal Growth Concepts, New York: Springer Verlag, 2010.

[9] Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. A. Dahmen, P. K. Liaw and Z. P. Lu, Microstructures and properties of high-entropy alloys, Prog. Mater. Sc, vol. 61, p. 1–93, 2014.