High Entropy Alloy Towards Functional Materials Application: A Review

Nur Izzi Muhammad Nadzri1, 2, Abhirah Khemar1, 2, Juyana A. Wahab1, 2, Mohd Muzamir Mahat1

1 Center of Excellence Geopolymer & Green Technology (CEGeoGTech), Universiti Malaysia Perlis, 02600, Arau, Perlis, Malaysia
2 Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, 02600, Arau, Perlis, Malaysia

Abstract The development of high entropy alloy (HEA) is considered a new bloom area as the ideas open up the exploration of a various multi-disciplinary elements in many applications. It is a novel class of complex materials identified in the phase diagram’s core, and they have been proven to outperform typical alloys. This HEA involves mixing unique combinations of mechanical and functional qualities across an infinite space of alloy composition. It is also possessing a great understanding of the thermodynamic behaviour of the materials which influence greatly their physical and mechanical properties. This review paper aims to open up the possibilities of developing HEA on different types of approaches based on the core effects which is very useful in functional materials applications especially in semiconductor, refractory and many more. However, to obtain this material, the most crucial thing is to understand and develop their synthesising routes of HEA production, which has become the main priority. Therefore, this paper focuses on discussing different metal elements that are commonly used in HEA and few fabrication routes on HEA. Some of recent functional materials based HEA is introduced by their enhance properties compare to conventional alloys.

1 Introduction

The discovery of alloy in term of design, and development is an integral feature of material research for industries like semiconductor, and energy generation and storage to develop [1–3]. Previously, the majority of conventional alloys are based on a single primary element. To increase the properties of the principle element, several alloying elements are added, resulting in an alloy family based on the principal element. This discipline of material science has proceeded further than the standard alloying system, which has one or two principal components, to a new class of highly alloyed materials known as high entropy alloys (HEAs). HEA was first introduced by Cantor [4] and Yeh [5] by which it was obtained by combining five or more elements with between 5 – 35 at. %. The combination of five or more different element in the materials introduced their solid solution states to have higher mixing entropies than conventional alloy. As a result, the entropy impact is significantly more apparent in HEAs. The findings show higher strength, ductility and other interesting properties of to this class that is due to their two or more consisting phases of microstructure which exhibit brittle intermetallic compounds [6]. From a physical metallurgy perspective, the existence of binary/ternary phase diagrams leads to multiple phases and intermetallic compounds that exhibit complex and brittle microstructures that are difficult to analyse and understand. However, because of this unique multi-principal element composition, extensive researches have been progressively carried out in other to have a better and in-depth understanding of these HEAs.

Some of the properties exhibit by HEAs are not seen in conventional alloys, such as being able to withstand high temperature which broadens the spectrum of application even further. According to King et al [7] the combination of these different elements will exhibit ductility and significant solid solution hardening, which will act as a stabiliser in a microstructure consisting of either (i) a single solid solution with one of the simple close-packed structures such as FCC, BCC or HCP or (ii) a duplex microstructure made up of two of these simple solid solutions. By combining a similar percentage of every element for HEAs, it will enable the crystal structure to be thermodynamically stable by which provide the existence of dislocation mobility and higher strength due to its large concentration of the element. One of the advantages of these HEA is the ability to be thermally stable while maintaining its ductility in low temperature. Therefore, this has sparked interest amongst researchers in exploring the possibility of HEA in the functional materials area. Some of the well-known functional materials HEAs are refractory HEAs, soft magnetic HEAs, corrosion resistance HEAs, superconducting HEAs and many more. However, in this paper, we will be focusing on discussing of the core effects of the HEAs development with few researches on the functional materials based HEAs.

In this paper, a review has made on the effects of different element compositions on the functionality of high entropy alloy with the selected interests of functional materials such as refractory materials and soft magnetic materials are being discussed. Besides, it has also navigates the current challenges and future directions of these HEAs.

2 High Entropy Alloy (HEA) core effects

From a thermodynamic approach, the effect of high entropy in favouring the development of simple solid solutions in HEAs may be an interesting approach to understand more about this material. The Gibbs free energy of mixing that a
reaction involves, which is measured by the manner in their concentration gradients are built up, determines the properties that can benefit from the mixture, which is calculated as

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \]  

Where the temperature is denoted as T, the energy change at constant pressure and temperature is measure by mixing enthalpy (\(\Delta H_{\text{mix}}\)) while \(\Delta S_{\text{mix}}\) stands for mixing entropy that measures a system’s randomness at the atomic level [4,5,8]. One of the key factors of notable properties of HEAs compared to their parent materials of the core effects. It has been highlighted by researchers [5,9,10] that four core elements which are the high entropy effect, lattice distortion, sluggish diffusion and lastly cocktail are the reason that affected the behaviour of the HEAs in material structures.

2.1 The high entropy effect

For HEAs, entropy mostly refers to configurational entropy by which the quinary random solid solution and stoichiometric intermetallic compounds is greatly influenced by the configurational entropy of an equimolar that is given 1.61R where R = 8.31J/K mol and zero, respectively. In HEA formation, random solid-solution phase easily occur rather than intermetallic phases [5,9,10]. This occur due to the lower Gibbs free energy in the HEAs. However, for the multi-component alloys, the high entropy effect does not guarantee the creation of a simple solid-solution phase. The five more elements of HEAs such as a combination between CoCuCrMnFeNi are highly likely to be in solid-solution phase rather than the intermetallic phase, according to the high entropy effect, which is the signature notion of HEAs. To validate this approach, idealised configurational entropy is compared to the entropy of fusion for pure metals or formation enthalpies of selected intermetallic compounds, which when comparing between these two phases, only configurational entropy is often considered [11].

The Gibbs Law suggested that the high entropy effect will decrease the stability of random solid solution phases with decreasing temperature. This is because, at low temperature of HEAs annealing, the randomized solid solution phases conceivably converted into metallic phases. One of the examples is the flow dynamics which has been discovered to be influenced not only by their strain rate and temperature but also their interior structural aspects [10,12]. Since it is difficult to differentiate structure features directly, the complex dynamics in the deformation process may help to understand the physical mechanism of the underlying microstructure of HEAs.

2.2 The lattice distortion effect

Significant lattice distortion is well presented in the structure with variation of atom sized that comprise the crystal lattices of intricate and whole phases The displacement at each lattice site is influenced by the atom that occupies that location or even the sorts of atoms in the surrounding environment. These distortions are said to be worse than those seen among typical alloys. The abundance structure in entropy is said to weakens X-ray diffraction peaks intensity, increase hardness and many more. These are dependent on the uncertainty in atom locations caused by these distortions. Lattice strain which is known to be proportional to the misfit parameter of atomic size difference in solid solution is suggested to be able to increase the strength and hardness when facing the solvent and solute atoms which is very hard to differentiate in HEAs [10,13,14]. However, the classic solid-solution strengthening model is rather difficult to distinguish. These statements appear to be physically plausible, but systematic attempts to quantify the majority of these impacts and isolate them from other factors have yet to be made. Fig. 1 shows a pure metal which is represented by a body centred cubic structure that has the same sort of atoms filling the lattice positions and thus creates no lattice distortion. However, when different element species were introduced to the structure, it generates minimal lattice deformation which creates different mechanical and physical properties of this material [15].

2.3 The sluggish diffusion effect

One of the reasons HEAs exhibit refractory property is because of their sluggish diffusion effect. During formation, when the diffusion amongst the elements in HEAs is slower than the conventional alloys, it is called the sluggish diffusion effect. Surrounding atoms of HEAs in each lattice is introduced to a greater variety of atoms when an atom migrates from one site to another, thus given higher normalised activation energy compared to conventional alloys by having extra free energy that occurs when two atoms that are opposed join together as interaction energy. Each lattice site in HEA has a separate set of atoms surrounding it. As a result, the overall interaction energy of each sites varies [8,16].

According to Tsai et al.[16], the diffusion kinetics of these HEAs is explainable by the single diffusion parameters. In contrast, Dabrowa et al.[17] and other researchers [18] suggested that the diffusion coefficients at high temperatures
has more influenced in term of the HEA crystalline structure compared to chemical environment formed by surrounding atoms [8].

![Lattice distortions schematics in body centred cubic pure metals and HEAs, where A to E represent different element species.](image1)

**Fig. 1:** Lattice distortions schematics in body centred cubic pure metals and HEAs, where A to E represent different element species.

### 2.4 The cocktail effect

Ranganathan [19] was the first to suggest the cocktail effect especially in HEAs. The original intention was just to create “a lovely, delightful blend” but it was then coming to denote as a synergistic mixture in which the ultimate outcome is unpredictable and greater than the sum of its part. Three types of alloys which are bulk metallic glasses, super-elastic and super plastic metals, and HEAs used this term to characterise them. This cocktail effect combines the amazing capabilities of totally amorphous bulk metallic glasses with the ultimate structural and functional properties of these metals to create a unique combination. The cocktail effect is inexorably tied to the composing materials when designing the element of mixture. The addition of light elements like Aluminium (Al) for example, able to reduce the density of HEAs. Meanwhile, high temperature characteristics can be improved by adding refractory materials such as Niobium (Nb).

The cocktail effect, unlike the other core effects, is not a theory and does not require confirmation. For example, Unpredictable synergistic response will be introduced near zero coefficients physical properties of thermal expansion or catalytic responses. In each of these circumstances, attributes are intricate and sensitively dependent on material composition, microstructure, electrical structure and other features. Many possibilities shall be arising from odd combinations of elements and microstructure composition based HEAs.

### 3 Functional Materials Based HEAs

#### 3.1 Refractory properties

Extensive researches have been conducted in refractory based HEAs. MoNbTaW is one of the popular HEAs for this purpose. A study conducted by Senkov et al. [20] demonstrated that HEA can withstand high temperatures while maintaining high specific strength. MoNbTaW and MoNbTaWV are few examples that possess the dendritic structure during plastic deformation at 1400°C. The microstructure of these materials showed that dislocation and boundary energy grains are dependent on dislocations and faults, which are the driving force for recrystallization. It was also found that after certain temperature, the amount of Nb, Mo and Ta has enriched compare to other elements [21].

Han et al [22] reported on the MoNbTaW development by pressureless spark sintering with the influence of ball milling. At a temperature below melting point, a BCC phase was obtained. The most important mechanism for atom movement in the production of high entropy solid solutions was evaluation condensation. The solid solution process for refractory metals was accomplished within 20 minutes without the existence of liquid phase. This is because submicron protrusions were created when the plasma refractory metals existed in the void areas of porous immediate products during sintering

Another interesting HEA based refractory material of NbTaTiV [23] reported to experience a connection between atoms and size mismatch which leads to an induced in the local severe lattice distortions. Comparing to the fully homogeneous sample, a lower effect on distortion is expected to occur in the chemical inhomogeneity of cast sample. This is greatly influenced by the configurational entropy method which is affected by the materials strengthening. However, both states of alloy have equal yield strength, which could be attributable to additional microstructural change between the as-cast and heat-treated alloys, such as grain size and the existence of residual stress during the casting process. Moreover, HfMoScTaZ refractory high entropy alloy [24] was prepared by vacuum arc melting route. It was
found that the alloy’s microstructure and composition are evenly dispersed and have a good balance of strength and toughness. At a temperature between 800°C to 1200°C, the compressive yield strengths are much stronger than other refractory materials.

3.2 High entropy films

The past few years, binary and/or ternary thin films have received a lot of attention. Conventional metal nitrides, carbides and oxide films, which are low entropy films, could not match the growing demand standards due to alloy entropy restrictions. HEA thin films are believed to not only have the same good performance like a bulk HEAs, but some of the properties have also been improved. These alloy films have significant potential in high hardness, corrosion resistant coatings and many more [25].

Some of the common routes for synthesising these films are chemical vapor deposition or physical vapour deposition. HEA thin films such as FeCrSiNb [26] which was synthesised by ion beam sputter deposition showed a dense and amorphous alloy. The fundamental reason for this is because of the transition from an ionic to solid state causes a considerable increase in cooling rate in the deposition chamber, releasing the condensation energy. Significant size differences may also contribute to the amorphization of HEA thin film. This high mixing entropy promotes mutual stability of various elements and prevents phase separation [27,28].

A novel combination of TaNbTiW thin film [29] was deposited by magnetron sputtering on silicon wafer which reported on the oxidation resistance aspect. It was reported that when the films were annealed at both 500°C and 700°C, the results of oxidation peaks are similar to the unannealed samples. Only a few oxide peaks emerge after annealing at 900. Two factors that could be ascribed to these behaviours which are (i) the Ti-W phase present in the sample with certain temperature has strong oxidation resistance, and (ii) the chemical mixing enthalpy of W-O is more positive than Ta-O and Nb. Thus, it implies that when percentage of Ti and W increases, the film grows more compact and denser, making oxygen ions diffusion into the films more difficult. This gave a new light to nitrides and oxynitride based HEA thin films to enhance the properties without being influence by oxidation easily compared to conventional metal nitrides/oxynitrides thin films.

4 Conclusions

HEA has been widely used to enhance the property of alloys and materials such as V and Ti. There has been significant progress of multiprincipal element alloy in the last 12 years. This continues to stimulate new research development especially in finding ways to face the challenges and obstacles of growing HEA based materials. Some of HEA have excellent properties such as excellent fatigue and wear resistance thus it is beneficial for sector like aerospace. Therefore, it is an interesting research subject to explore and understand the HEA physically and mechanically as it will open up a new approach on the functional materials applications.

References

1. D. J. M. Kim, S. T. Y. Cheung, S. A. Humphy-Baker et al, Acta Mater. 166 (2019)
2. S. I. Rao, B. Akdim, E. Antillon, C. Woodward, T. A. Parthasarathy, O. N. Senkov, Acta Mater. 168 (2019)
3. B. S. Murty, J. W. Yeh, S. Ranganathan & P. P. Bhattacharjee, Acta Mater. 2 (2019)
4. B. Cantor, Entropy 16 (2014)
5. J. W. Yeh, Elsevier (2021)
6. B. S. Murty, J. W. Yeh, S. Ranganathan & P. P. Bhattacharjee, Elsevier 2 (2019)
7. D. J. M. Kim, S. C. Middleburgh, A. G. McGregor & M. B. Cortie, Acta Mater. 104 (2016)
8. P. Z. Lu, H. Wang, M. W. Chen, Intermetallics 66 (2015)
9. D. B. Miracle & O. N. Senkov, Acta Mater. 122 (2017)
10. J. Chen, X. Zhou, W. Wang et al., J. Alloys Compd. 760 (2018)
11. P. Sharma, V. K. Dwivedi, S. P. Dwivedi, Mater Today Proc. 43 (2020)
12. Q. Zhou, Y. Du, W. Han, Q. Jia, Y. Deng, H. Wang, Mater Des. 189 (2020)
13. Basu, J. T. M. De Hosson, Scr. Mater. 187 (2020)
14. B. S. Murty, J. W. Yeh, S. Ranganathan, P. P Bhattacharjee, Elsevier 2 (2019)
15. W. Li, D. Xie, D. Li, Y. Zhang, Y. Gao, P. K. Liaw, Prog. Mater. Sci. 118 (2021)
16. M. H. Tsai, Entropy 15 (2013)
17. J. Dąbrowa, W. Kucza, G. Cieślak, T. Kulik, M. Danielewski, J. W. Yeh, J. Alloys Compd. 674 (2016)
18. W. Kucza, J. Dąbrowa, G. Cieślak, K. Berent, T. Kulik, M. Danielewski, J. Alloys Compd. 731 (2018)
19. S. Ranganathan, Curr Sci, 85 (2003)
20. O. N. Senkov & C. F. Woodward, Mater Sci Eng A. 529 (2011)
21. O. N. Senkov, S. Rao, K. J. Chaput, C. Woodward, Acta Mater. 151 (2018)
22. J. Han, B. Su, J. Lu, J. Meng, A. Zhang, Y. Wu, Intermetallics 123 (2020)
23. C. Lee, G. Song, M. C. Gao et al., Acta Mater. 160 (2018)
24. X. W. Nie, M. D. Cai, S. Cai, Int J Refract Met Hard Mater. 98 (2021)
25. X. H. Yan, J. S. Li, W. R. Zhang, Y. Zhang, Mater Chem Phys. 10 (2018)
26. W. Mufiah, J. Allport, V. Vishnyakov, Surf Coatings Technol. 422 (2021)
27. S. Guo, Q. Hu, C. Ng, C. T. Liu, Intermetallics 41 (2013)
28. B. R. Braeckman, D. Depla, J. Alloys Compd. 646 (2015)
29. Y. Zhang, T. Zuo, Z. Tang et al., Prog. In Mat. Sc. 61 (2014)