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HIGH ENTROPY ALLOY AND THEIR FUTURE PROSPECTS

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ABSTRACT

A conventional alloy containing a single metal as a base, like steels, aluminium alloys, titanium alloys and nickel alloys, remains a focus of researchers working on metallic materials in the 20th century to tailor physical, mechanical, and chemical properties for a wide range of engineering applications. The increasing demand for structural integrity, damage tolerance, durability, and high-temperature stability for advanced aerospace, automotive, marine, and power engineering applications urges the invention of new metallic materials triggered in the 21st century. Hence, a new era began from reporting the nonconventional approach of alloy design in 2004 by Brain Cantor and Jien-Wei Yeh, containing multi-principal elements exhibiting stable solid solution phases via higher intrinsic mixing entropy. These alloys consist of transition elements, alkali metals, alkaline earth metals, metalloids, refractory metals, and nonmetals but in higher atomic concentrations. High entropy alloys are classified into four types containing solid solutions with arbitrary crystal structures like FCC, BCC, HCP or multiple solid solutions. It will overview their classes and prospects concerning advanced engineering applications.

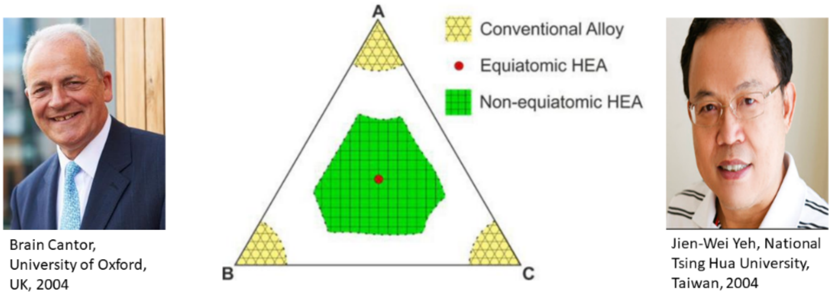
KEYWORD

High entropy alloys, Transition metals, Refractory metals, Strength and Ductility trade-off, Oxidation resistance, Corrosion resistance

INTRODUCTION

Metallic materials account for a sizable share of engineering applications. The conventional alloy design idea includes one element as the foundation of the alloy and the rest of the elements as major and minor alloying additions, with a few microalloyings and modifiers also employed as specialized property enhancers. Since the revolutionary new notion of multi-principal element alloys was introduced in 2004 by Brain Cantor et al. and Yeh et al., a new road to the design of millions of novel alloys has been opened (Cantor, Chang, Knight, & Vincent, 2004; J. W. Yeh et al., 2004).

These alloy systems are distinguished from normal alloys by four fundamental effects that do not occur in typical alloy systems: high mixing entropy of elements, severe lattice distortion in the crystal structure, sluggish diffusion, and cocktail effect. These alloy systems are later referred to officially as high entropy alloys (HEA). Instead of the weight percentages used in standard alloy system design, the novel notion of focusing on tailoring high entropy crystal structure atomic proportion of intermixing is stressed. HEAs often feature five or more major components. According to Yeh et al., high entropy alloys are referred to as alloys containing the concentration of the primary components, which is normally between 5 at. % and 35 at. %, whereas the minor elements should be less than 5 at. % (J.-W. Yeh, 2013).



Brain Cantor, University of Oxford, UK, 2004

Jien-Wei Yeh, National Tsing Hua University, Taiwan, 2004

Figure 1: Equimolar or nearly equimolar multi-element alloy concept (Cantor et al., 2004; J. W. Yeh et al., 2004)

Empirical phase stability in high entropy alloys is gauged by thermodynamic and geometric factors.

$$\Delta G_{mix} = \sum_{i=j,i\neq j}^{n} \Omega_{ij} C_i C_j$$

Where $4\Delta H_{ij}^{mix}$ is the enthalpy of mixing at the equimolar composition of binary liquid alloys computed using Miedima's model and $\Omega ij = 4\Delta H_{ij}^{mix}$ the regular solution interaction parameter between the i^{th} and j^{th} components.

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$$

Where $T_m = \sum_{i=1}^{n} C_i (T_m)_i$, $(T_m)_i$ is the melting point of i^{th} element.

$$\delta_r = \sqrt{\sum_{i=1}^{n} C_i (1 - \frac{r_i}{\bar{r}})^2}$$

Where $\bar{r} = \sum_{i=1}^{n} C_i r_i$ C_i and r_i are the atomic percentage and radius of i^{th} element.

$$\frac{e}{a} = \sum_{i=1}^{n} C_i (e/a)_i$$

$$VEC = \sum C_i (VEC_i)$$

where $(e/a)_i$, VEC_i, and C_i represent the valance electron concentration and atomic proportion of the respective elements, respectively.

$$\Delta\chi = \sqrt{\sum_{i=1}^{n} C_i (\chi_i - \bar{\chi})^2}$$

Where $\chi = \sum_{i=1}^{n} C_i \chi_i, \chi_i$ is Pauling electronegativity of the i^{th} element. Figure 2 represents the threshold values corresponding to solid solution stability canvas in high entropy alloys.

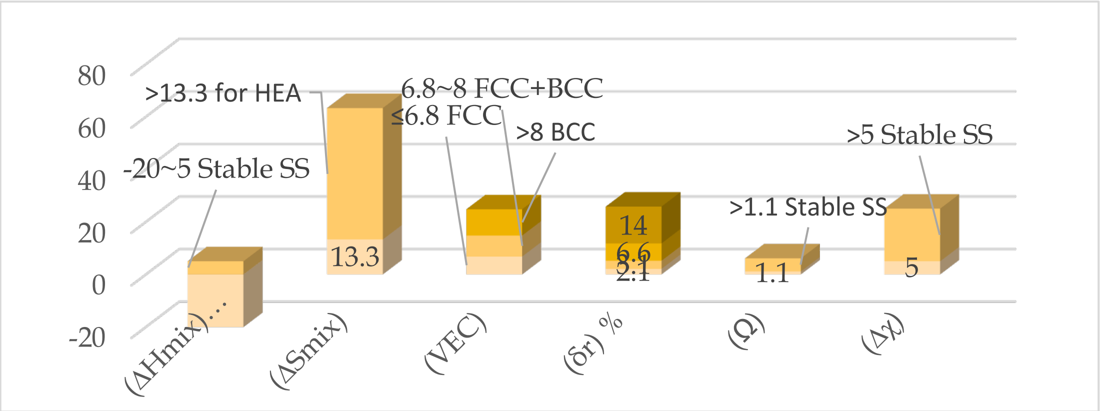


Figure 2: Empirical solid solution phase stability canvas

Transition Metals High Entropy Alloys (THEA)

Yeh et al. reported multiple equimolar high entropy alloy systems in 2004; AlCoCrFeNi is one of them. Since then, parallel to Cantor's alloy, it has been extensively investigated in terms of methodologies of its manufacturing, phases and structure, thermal phase transformations, deformation, corrosion resistance, magnetic, mechanical, and tribological properties. Manufacturing methods, induction melting (IM), vacuum induction melting (VIM) vacuum arc melting (VAR), Induction levitation melting (ILM) spark plasma sintering (SPS) and selective laser melting (SLM), and their process parameters have a significant impact on structure and properties of high entropy alloys.

Tian et al. manufactured through induction levitation melting (ILM) and arc melting. Induction levitation melted samples exhibited better yield strength (1631 vs. 1209 MPa) and microhardness (519 vs. 493 HV). To overcome the segregation problem of casting, a powder metallurgy route consisting of mechanical alloying and sintering is often preferred (Tian et al., 2019).

Zhang et al. reported the influence of varying spark plasma sintering temperatures on the microstructure and mechanical properties of AlCoCrFeNi alloy. He concluded that with increasing sintering temperature, Al-Ni depleted FCC phase formation increases, and BCC phase transformation from Cr-Fe rich to Cr-rich triggers within B2. With increasing sintering temperature from 1100 ^{0}C to 1250 ^{0}C, yield strength decreases from 2368 MPa to 1626 MPa, while other samples at 1250 ^{0}C decreased further to 1262 MPa (Zhang, Han, Meng, Su, & Li, 2016). Figure 3 illustrates the strength and ductility synergy in high entropy alloys compared to conventional alloys like aluminium alloys, magnesium alloy, and steels. Secondly, their ability to withstand high temperature service conditions without losing their strength compared to conventional nickel alloys Inconel 718 and Haynes 230 encourages high-tech applications.

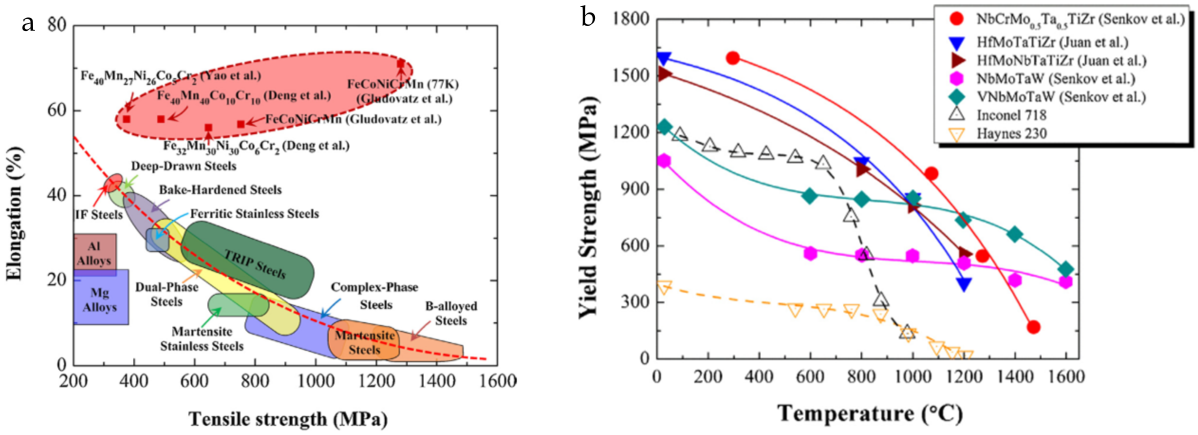


Figure 3: a) Strength and ductility trade-off b) High-temperature stability (Ye, Wang, Lu, Liu, & Yang, 2016)

Refractory High Entropy Alloys (RHEA)

RHEAs are considered potential high-temperature application materials because of their good mechanical capabilities at increased temperatures. They are appropriate for complicated service situations like those in nuclear energy power plants, aerospace, military, and sophisticated manufacturing industries. The first published report regarding refractory high entropy alloys (RHEA) in 2010 gained attention from scientists and researchers due to their promising mechanical strength at high temperatures of 1600 ^{0}C. RHEAs are crafted initially on five refractory elements (Mo, Nb, Ta, V, and W), and afterwards, five refractory elements (Ti, Zr, Hf, Cr, and Re) are added. Afterwards, a trace quantity of non-refractory metal components, such as Al, Si, Co, or Ni, is added to enhance its overall qualities. RHEA preparation processes are more limited than other HEAs due to the high melting temperatures of the RHEA's component elements. Arc melting and powder metallurgy are the primary methods of producing bulk RHEAs. Arc melting with highpurity argon has been used to effectively produce many RHEAs, including HfNbTiZr, HfZrTiTa0.53, and NbZrTiCrAl RHEAs with single-phase BCC. The dendrite and interdendritic zones of NbZrTiCrAl RHEAs have an uneven microstructure. While Al, Cr, and Zr are mostly dispersed in the interdendritic, Nb and Ti are mostly distributed in the dendrites (Wang et al., 2023).

Arc melting has the benefit that, because of its high melting temperature, it can efficiently remove volatile contaminants. The technique works well for making RHEAs with high melting points. However, there will be significant composition segregation during the melting process since RHEAs have a complex composition of component elements with high melting temperatures. As a result, chemical segregation, such as dendritic microstructure, may be primarily decreased by increasing the solidification rate, subjecting materials to extended high-temperature heat treatment, or changing their chemical compositions (George, Raabe, & Ritchie, 2019).

FUTURE PROSPECTS

Higher fracture toughness, strength and ductility synergy favour their applicability in dynamic service parts to meet the damage tolerance. Appreciable corrosion resistance and high-temperature oxidation resistance fulfil the chemical, power and aerospace sector requirements. However, low-density, high entropy alloys with higher specific strength meet the transportation industry requirements for manufacturing critical parts.

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