High Entropy Alloys for Extreme Load-Bearing Applications

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Abstract

High entropy alloys (HEAs) have emerged as a new class of materials that can exhibit superior mechanical properties to the conventional alloy systems. Therefore, they are promising candidates as the next generation structural materials. As the studies into the HEAs deepen, the original proposal of equal concentration of each element while remaining a single phased structure has been expanded and new opportunities start to emerge. Here we briefly discuss several future directions for HEAs which include fundamental questions such as chemical short-range order and synergistic strengthening mechanisms, as well as HEA's potential applications under extreme conditions such as high-temperature and cryogenic load-bearing, impact protection and kinetic penetrator.

Key words: High entropy alloys; Materials under extreme conditions; Refractory metals

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1 Introduction

The ever more extreme service conditions have posed significant challenges on the structural materials that are currently available off the shelf. For example, the rapid development of aerospace industry demands more powerful jet engines, which calls for new materials that can sustain higher temperatures. The opposite extreme is materials that do not fracture easily under low-to-cryogenic temperatures, which can find applications in deep-sea and deep-space explorations. In fusion reactors, the "hot plasma" must be generated and confined for sufficiently long time to ignite fusion reactions, thus subjecting the plasma facing materials to a highly corrosive and high temperature environment. On top of these extreme material selection criteria, lightweight structural materials are always of pursuit in practically every engineering fields. Therefore, we need stronger, tougher, lighter and more heat-resistant materials to meet these challenges. The question naturally arises as to what the structural materials will be used for the future. Although the answer is still vague, several directions can be laid out which can potentially offer solutions for extreme applications.

2 The concept and developments of high entropy alloy

The most widely used approach to tailor the mechanical behavior of materials is via metallurgical alloying in which different chemical species can play different roles. Such strategies dates back to thousands of years ago since metals become the primary tool for human beings. In recent decades, the advance of high entropy alloys (HEA), or multiple principal element alloys, have drawn massive research interests ever since the pioneering work of Yeh and Cantor[1,2]. Contrary to the conventional alloy design strategies which only use single principal element and minor amounts of other constitutes, HEAs often involve multiple elements with equal- or near equal-atomic ratio, which pushes our understandings of phase equilibria to its limit[3]. As a result, the highly concentrated alloys exhibit some distinctive properties that can cater to the extreme conditions. Currently, the most widely studied HEAs can be classified into two major groups (shown in Fig. 1), the transition metal based, face centered cubic structured family and the refractory metals based, body centered cubic structured family.

The transition metals-based alloys often acquire a FCC structure with low stacking fault energy, which ensures their sustained strain hardening ability and strain rate hardening ability. It has been reported that the classical equal-atomic CrMnFeCoNi high entropy alloy (the Cantor alloy) exhibits an excellent strain hardening ability within a wide temperature range. Especially, both strength and fracture toughness of the alloy are higher at 77 K than the ambient condition, owing to the enhanced twinning ability at reduced temperatures[4]. Another important merit of the FCC HEAs is its excellent impact resistance, which is attributed to the strong strain rate hardening of the material.

In addition to the FCC high entropy alloys, refractory metals based, BCC high entropy alloys (often termed as RHEA) receive more attention in recent years due to their potential to

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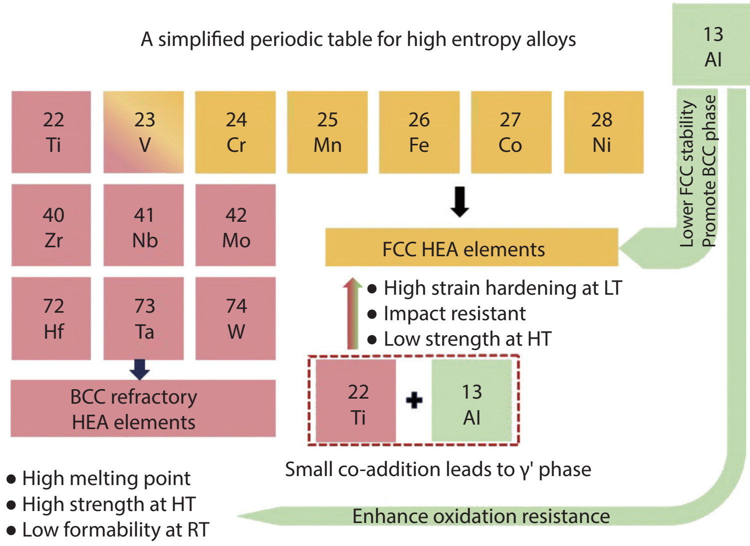

Fig. 1 A simplified periodic table for the high entropy alloys with a focus on transition metals-based FCC family and refractory metals-based BCC family. Note that there are other HEAs with less common elements which are not included in this diagram.

be used at elevated temperatures. The rationale is simply that RHEAs often acquire remarkably high melting points (often > 1600 °C). Typical examples are NbMoTaW and NbMoTaVW alloys which were designed by Senkov and co-workers[5]. Some RHEAs can achieve remarkable strength at elevated temperatures up to 1600 °C, which is far beyond the melting point of Ni-based superalloys. For instance, the NbMoTaVW alloy displays an impressive yield strength (compressive) of 500 MPa at 1600 °C, showing great potential for high temperature applications[6]. It has been shown that adding Al to the RHEA system can further improve the strength as well as the oxidation resistance of the materials. However, the materials become progressively brittle[7].

3 Future directions and challenges

The emergence of HEA has dramatically expanded the chemical space of the alloy design, thus providing numerous opportunities to solve the ground challenges we will be facing in the future. Regardless of the promises, there are important scientific problems need to be clarified and HEAs with better mechanical properties need to be designed.

3.1 The elemental distribution within HEA is non-trivial and needs to be deciphered

For example, chemical short-range order (SRO) and/or local chemical fluctuation exists in the previously presumed disordered lattice[8–12], which lowers the configurational entropy and challenge the original concept of HEA. Although more and more evidence has confirmed the existence of such a subtle chemical heterogeneity, much more need to be done to understand the thermodynamics, the spatial distribution, and the complex effects of SRO on the physical and mechanical properties of the materials. For example, the driving force and the kinetics of the formation of the SRO is still unknown. Since SROs only involves a couple of nearest neighbor distance, it is difficult to resolve their structural or chemical identity. With the advance of modern characterization techniques such as energy filtered electron microscopy, atomic electron tomography and atomic probe tomography, these puzzles are expected to be solved in the future. Understanding the chemical heterogeneity in these complex concentrated alloy systems can facilitate designing better HEAs with extraordinary mechanical behavior[13].

3.2 Incorporation of multiple strengthening mechanisms in a single FCC HEA

The versatile deformation mechanisms render many transitions metals-based FCC HEAs to be ductile and crack-resistant. However, their yield strengths of the as-casted alloys are somewhat mediocre, which limits its applications in extreme conditions. Therefore, improving the yield strength of FCC HEAs is of technological importance. Many efforts have been devoted in this aspect; the primary goal is to incorporate as many deformation mechanisms as possible in a single alloy system. For example, one can take the advantage of the sustained strain hardening ability of the CrMnFeCoNi related FCC alloys and impose significant cold work into the material, which may sacrifice the ductility but can achieve high strength. Further reducing the stacking fault energy by deviating the composition away from equal-atomic ratio can affect the phase stability of the alloy and can further promote their mechanical properties. Based on this strategy, the metastability engineering of the CrCoNi-based alloy has become a viable approach to achieve better mechanical properties[14]. For example, some non-equal-atomic HEAs can both display strong twinning induced plasticity (TWIP), transformation induced plasticity (TRIP) and even amorphization[15], which improve the strength-ductility synergy of these HEAs. Another strengthening mechanism is precipitation hardening where an analogy to the Ni-based superalloy can be drawn for the FCC HEAs. For example, Yang and co-workers[16] introduced Ti and Al into the FCC HEA and obtained the ordered phase strengthened HEA where both the disordered matrix and the order precipitates (γ') are of "high-entropy" in nature. In addition to these "conventional strengthening mechanisms", microstructure design is another viable route for achieving better mechanical properties. In this regard, as pointed it out by

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Ma and Wu[17], engineering HEA with heterogeneous structures can further promote strength and ductility. Recently, Pan[18] introduced a gradient cell-structured HEA which indeed achieved a much improved strength-ductility synergy compared with the pristine material. In the future, how to incorporate different types of strengthening mechanisms in a single material (or part) remain to be an outstanding challenge. Additive manufacturing perhaps is the utmost solution where gradient structures and chemistry can be precisely introduced in a single part.

3.3 Enhancing the tensile ductility of the RHEA at ambient temperature

Some RHEAs (especially those W-containing ones) can display outstanding strength at elevated temperatures[19,20]. However, the much-reduced tensile ductility at ambient temperature limits the applications of these systems. The origin of the room temperature brittleness is still a mystery to be solved. But it must have to do with dislocation dynamics[21]. The complex energy landscape for the RHEAs renders the configuration of dislocations distinctive to the dilute BCC alloys. None-screw dislocations can play a crucial role in these materials[21]. Interstitials can also affect the dislocation pattern in Ti-containing RHEAs. For instance, Lei *et al.*, demonstrates that by doping the model TiZrHfNb RHEA with 2 percent of oxygen, a planar-to-wavy dislocation slip transition can be observed, and the room temperature ductility is enhanced[22]. Going forward, much more need to be done to understand the fundamentals of dislocation in the RHEAs, which require correlative in-situ microscopy with first principal simulations. As for the practical application, the biggest challenge for the RHEA is to overcome the tradeoff between high temperature strength and room temperature formability. In this frontier, it still seems unclear as to what is the right alloy system that can be used in the future. The chemical space of the RHEA is huge, and we are only scratching the surface. With the aid of high throughput experiment as well as machine learning-based alloy screening strategies[23], we are on the verge to make a breakthrough.

3.4 Investigation and application of the HEAs at high strain rates

In recent years, the behavior of HEAs at elevated strain rate starts to receive massive attentions. Such scenarios can typically be found in either kinetic energy penetrator or armor protection. For example, 'Self-sharpening' is an ability of the alloy retaining the sharp head during dynamic penetration mainly due to the adiabatic shear localization. Traditional heavy-tungsten alloys containing the principal tungsten element have been used as the kinetic energy penetrator due to its high strength and high density. However, its poor plasticity limits its penetration performance. Recently, WFeNiMo high-entropy alloy was created to have much better penetration ability due to its high strength (~1.9 GPa) and the susceptibility to shear localization[24]. The presence of the strong μ phase precipitations results in inhomogeneous deformation and strain gradients between them and FCC matrix. These stored deformation energy drives the dynamic recrystallization softening and triggers the formation of shear bands easily. Liu *et al.*[25] developed a novel high density Fe-22W-13.3Ni-6.8Mo-6.5Co steel obtaining high strength ~2.3 GPa and good plasticity under dynamic loading, which can be served as the low-cost penetrator. The micro-sized μ phases in it can be resolved into the BCC matrix during shear localization process. By optimizing the chemical composition and microstructure of these HEAs, the anti-armor capacity can be raised significantly. In contrast, the resistance of shear localization has been revealed in the CrCoNi-based high-entropy alloys to a large forced shear strain ~7 bearing high strain-rate 10^3-10^5 s^{-1} load[26]. The CrCoNi-based alloys shows extraordinary strain hardening rate over 1000 MPa until the shear failure. This was mainly attributed to the multiple strengthening mechanisms such as forest dislocation sliding, nano-twining and even phase transformation[27]. Due to smaller activation volume for the dislocation motion, the strain-rate sensitivity of HEAs is relatively larger than that of conventional alloys. The high strain hardening rate and high strain-rate sensitivity overcomes the thermal softening effect under dynamic loading in the CrCoNi-based HEAs, which retards the shear localization failure. To work as an impact-resistance material, microstructural design such as defect engineering can be applied to increase strength, and incorporating alloy elements that can reduce the stacking-fault energy may give rise to higher strain hardening ability of CrCoNi-based HEAs. Spall failure of HEAs under dynamic impact cannot be ignored for defense applications. Hawkins *et al.*[28] conducted a series of shock loading experiments with projectile speed 300 m s^{-1} on FeCrMnNi HEA. It concludes that the compressive strength is not high enough although the spall strength is relatively high ~1.9 GPa. Thus, they suggest using a higher compressive strength HEAs for potential armor applications. Thürmer *et al.*[29] found the exceptional high spall strength of the Cantor alloy ~8 GPa at 10^7 s^{-1}, which is comparable to the strong BCC material like Ta. Profound amounts of nano-twins were discovered to resist crack-propagation. Jian *et al.*[30] utilized the molecular dynamics simulation method to study the possible amorphization behavior in CrCoNi medium-entropy alloy. At high velocity 1200-1400 m s^{-1}, the lattice distortion promotes the amorphization, resulting in a lower spall strength. It is still not clear how local chemical composition change may influence the deformation and failure behavior of the HEAs at the extreme strain-rate $>10^5$ s^{-1}. More systems need to be explored for the development of next generation amor.

3.5 Lightweight high-entropy alloys

Reduction of density is a critical issue for the application of HEAs in the areas of automobile, aerospace, and fossil energy. Most of low density HEAs were synthesized with Al, Mg, and Ti elements and often obtained secondary phases. A lightweight $Ti_3V_2ZrNbMo_{0.05}$ HEA with high yield stress and sufficient ductility was developed by mixing ductile BCC matrix and strong ultrafine- or nano-sized intermetallic compound particles[31]. In addition to this, by taking advantaging of CALPHAD-based high-throughput computational method to eliminate detrimental intermetallic phases, Feng *et al.*[32] found a lightweight Al-Cr-Fe-Mn-Ti HEA with high-density coherent $L2_1$ precipitates, achieving an extraordinary tensile yield strength ~2 GPa and failure strain ~30%. Incorporating non-metallic elements such as B, C, N, and O would be an alternative low-cost way to improve the strength of lightweight HEAs in the future[33].

4 Concluding remarks

The concept of high entropy alloys indeed opens a door to the new world for alloy design and many interesting materials continuously being proposed almost everyday in the labs all around the world[34]. For example, Xie recently designed FCC/Laves eutectic high-entropy alloys where the Lavas phases keep strengthening through the obstacle-defect interaction to a large fracture strength over 2 GPa[35]. However, the application of high entropy alloys still needs to be explored. The major roadblock that hinters the applications of the HEAs lies in the fact that they are remarkably more expensive than the commercial alloys. Moreover, the complex composition renders the expensive elements used in HEAs extremely challenging to be recycled, which, in turn, increases the cost of the materials. Therefore, the most promising applications for HEAs are those extreme ones where expense are not usually of the primary concern. Significant efforts are required to choose economically feasible and environmental-friendly alloys that meet green, low-carbon, and technical standards nowadays[36]. This perspective only provides, but not limits to, several future directions in this vibrating field. There are, of course, other important aspects of HEA such as their excellent radiation-resistance, which is beneficial for next generation fission reactors[37].

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

The manuscript was drafted by Prof. Shiteng Zhao and Prof. Zezhou Li. All authors had approved the final version of the manuscript.

REFERENCES

1. J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang, *Advanced Engineering Materials*, 2004, 6, 299
2. B. Cantor, I. T. H. Chang, P. Knight and A. J. B. Vincent, *Materials Science and Engineering: A*, 2004, 375−377, 213
3. Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. A. Dahmen, P. K. Liaw and Z. P. Lu, *Progress in Materials Science*, 2014, 61, 1
4. B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George and R. O. Ritchie, *Science*, 2014, 345, 1153
5. O. N. Senkov, G. B. Wilks, D. B. Miracle, C. P. Chuang and P. K. Liaw, *Intermetallics*, 2010, 18, 1758
6. O. N. Senkov, G. B. Wilks, J. M. Scott and D. B. Miracle, *Intermetallics*, 2011, 19, 698
7. D. B. Miracle, J. D. Miller, O. N. Senkov, C. Woodward, M. D. Uchic and J. Tiley, *Entropy*, 2014, 16, 494
8. J. Ding, Q. Yu, M. Asta and R. O. Ritchie, *Proc. Natl. Aca. Sci. U. S. A.*, 2018, 115, 8919
9. R. Zhang, S. Zhao, J. Ding, Y. Chong, T. Jia, C. Ophus, M. Asta, R. O. Ritchie and A. M. Minor, *Nature*, 2020, 581, 283
10. Q. Ding, Y. Zhang, X. Chen, X. Fu, D. Chen, S. Chen, L. Gu, F. Wei, H. Bei, Y. Gao, M. Wen, J. Li, Z. Zhang, T. Zhu, O. Ritchie and Q. Yu, *Nature*, 2019, 574, 223
11. X. Chen, Q. Wang, Z. Cheng, M. Zhu, H. Zhou, P. Jiang, L. Zhou, Q. Xue, F. Yuan, J. Zhu, X. Wu and E. Ma, *Nature*, 2021, 592, 712
12. Y. Ma, Q. Wang, C. Li, L. J. Santodonato, M. Feygenson, C. Dong and P. K. Liaw, *Scripta Materialia*, 2018, 144, 64
13. H. Li, H. Zong, S. Li, S. Jin, Y. Chen, M. J. Cabral, B. Chen, Q. Huang, Y. Chen, Y. Ren, K. Yu, S. Han, X. Ding, G. Sha, J. Lian, X. Liao, E. Ma and J. Sun, *Nature*, 2022, 604, 273
14. Z. Li, K. G. Pradeep, Y. Deng, D. Raabe and C. C. Tasan, *Nature*, 2016, 534, 227
15. K. Ming, W. Lu, Z. Li, X. Bi and J. Wang, *Acta Materialia*, 2020, 188, 354
16. T. Yang, Y. L. Zhao, Y. Tong, Z. B. Jiao, J. Wei, J. X. Cai, X. D. Han, D. Chen, A. Hu, J. J. Kai, K. Lu, Y. Liu and C. T. Liu, *Science*, 2018, 362, 933
17. E. Ma and X. Wu, *Nature Communications*, 2019, 10, 5623
18. Q. Pan, L. Zhang, R. Feng, Q. Lu, K. An, A. C. Chuang, J. D. Poplawsky, P. K. Liaw and L. Lu, *Science*, 2021, 374, 984
19. C. Lee, G. Kim, Y. Chou, B. L. Musicó, M. C. Gao, K. An, G. Song, Y.-C. Chou, V. Keppens, W. Chen and P. K. Liaw, *Science Advances*, 2020, 6, eaaz4748
20. S. Wei, S. J. Kim, J. Kang, Y. Zhang, Y. Zhang, T. Furuhara, E. S. Park, C. C. Tasan, *Nature Materials*, 2020, 19, 1175
21. F. Wang, G. H. Balbus, S. Xu, Y. Su, J. Shin, P. F. Rottmann, K. E. Knipling, J.-C. Stinville, L. H. Mills, O. N. Senkov, I. J. Beyerlein, T. M. Pollock and D. S. Gianola, *Science*, 2020, 370, 95
22. Z. Lei, X. Liu, Y. Wu, H. Wang, S. Jiang, S. Wang, X. Hui, Y. Wu, B. Gault, P. Kontis, D. Raabe, L. Gu, Q. Zhang, H. Chen, H. Wang, J. Liu, K. An, Q. Zeng, T.-G. Nieh and Z. Lu, *Nature*, 2018, 563, 546
23. W. Huang, P. Martin and H. L. Zhuang, *Acta Materialia*, 2019, 169, 225
24. X. F. Liu, Z. L. Tian, X. F. Zhang, H. H. Chen, T. W. Liu, Y. Chen, Y. J. Wang, L. H. Dai, *Acta Materialia*, 2020, 186, 257
25. A. Liu, L. Wang, L. Pan, X. Cheng, *Materials Science and Engineering: A*, 2021, 824, 141797
26. Z. Li, S. Zhao, S. M. Alotaibi, Y. Liu B. Wang, M. A. Meyers, *Acta Materialia*, 2018, 151, 424
27. S. Zhao, Z. Li, C. Zhu, W. Yang, Z. Zhang, D. E. Armstrong, P. S. Grant, R. O. Ritchie, *Science Advances*, 2021, 7, eabb3108
28. M. C. Hawkins, S. Thomas, R. Hixson, J. Gigax, N. Li, C. Liu, J. A. Valdez, S. Fensin, *Materials Science and Engineering: A*, 2022, 840, 142906
29. D. Thürmer, S. Zhao, O. R. Deluigi, C. Stan, I. A. Alhafez, H. M. Urbassek, M. A. Meyers, E. M. Bringa, N. Gunkelmann, *Journal of Alloys and Compounds*, 2022, 895, 162567
30. W. R. Jian, Z. Xie, S. Xu, X. Yao, I. J. Beyerlein, *Scripta Materialia*, 2022, 209, 114379
31. Y. Jia, G. Wang, S. Wu, Y. Mu, Y. Yi, Y. Jia, P. K. Liaw, T. Zhang, C.-T. Liu, *Applied Materials Today*, 2022, 27, 101429
32. R. Feng, C. Zhang, M. C. Gao, Z. Pei, F. Zhang, Y. Chen, D. Ma, K. An, J. D. Poplawsky, L. Ouyang, Y. Ren, J. A. Hawk, M. Widom, P. K. Liaw, *Nature Communications*, 2021, 12, 4329
33. O. Maulik, D. Kumar, S. Kumar, S. K. Dewangan, V. Kumar, *Materials Research Express*, 2018, 5, 052001
34. Y. Zhang, Amorphous Alloys and High Entropy Materials, Viser Technology, Singapore, 2022.
35. T. Xie, Z. Xiong, Z. Liu, G. Deng, X. Cheng, *Materials & Design*, 2021, 202, 109569
36. J. L. Cann, A. De Luca, D. C. Dunand, D. Dye, D. B. Miracle, H. S. Oh, E. A. Olivetti, T. M. Pollock, W. J. Poole, R. Yang, C. C. Tasan, *Progress in Materials Science*, 2021, 117, 100722
37. C. Lu, L. Niu, N. Chen, K. Jin, T. Yang, P. Xiu, Y. Zhang, F. Gao, H. Bei, S. Shi, M.-R. He, I. M. Robertson, W. J. Weber, L. Wang, *Nature Communications*, 2016, 7, 13564

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