



Review

Solving the strength-ductility trade-off using complex concentrated alloy design strategy: An overview

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ABSTRACT

This review provides a comprehensive assessment of recent advances in overcoming strength–ductility trade-off in structural alloys through the design of complex concentrated alloys (CCAs) and high entropy alloys (HEAs). It integrates a bibliometric analysis (2014–2024) with a mechanistic evaluation of emerging strategies, emphasizing transition metal-based systems. Findings from over 2,200 publications highlight growing global collaboration, dominant research clusters, and underexplored domains such as TRIP/TWIP effects and interstitial strengthening. Mechanistically, the review consolidates insights into solid solution, grain boundary, dislocation, precipitation, and interstitial strengthening; together with advanced mechanisms including stacking fault engineering, phase metastability, and heterostructural design. Emphasis is placed on the synergistic operation of these mechanisms especially TWIP/TRIP and back-stress hardening, to achieve superior strength–ductility combinations. Distinctions between HEAs and CCAs are clarified, and quantitative contributions of each strengthening mechanism are mapped. The role of hydrogen effects, additive manufacturing, and multi-scale processing in tailoring properties are discussed. By synthesizing bibliometric trends and mechanistic principles, this review establishes a roadmap for future alloy design strategies, offering a robust framework to guide the development of next-generation structural materials with multifunctional performance attributes.

1. Introduction

Structural materials are the foundation of modern engineering. They provide the essential framework for critical systems in transportation, infrastructure, energy, water, healthcare, and advanced manufacturing. From vehicles and aircraft to buildings and bridges, their integrity is vital to safety and performance [1–7]. As we address global challenges in sustainability and resource efficiency, these multifunctional materials are key drivers of economic growth and innovation. The development of damage-tolerant materials is increasingly crucial, enabling lighter vehicles, safer infrastructure, and more efficient power systems [1,8–19]. Meeting the demands of 21st - century engineering requires materials that have property (e.g., strength – ductility) synergy [13,20–39]. This

combination is generally difficult to achieve in conventional alloys due to intrinsic trade-offs [26,28,40–43] and inherent shortcomings associated with the design philosophy.

Traditional alloy design strategies have explored various methods to enhance both strength and ductility. This is mainly through compositional adjustments [44–51] and microstructural engineering [52–57]. Techniques such as heat treatment and grain boundary manipulation have been used to strengthen alloys by hindering dislocation movement, a characteristic Hall-Petch effect [58–66]. However, these approaches often result in a trade-off where the increase in strength leads to a significant loss of ductility [26,28,40–43,67,68]. This inverse relationship is commonly represented by a banana-shaped curve on a strength-ductility plot, highlighting the difficulty of achieving high

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levels of both properties simultaneously in conventional alloys.

The next generation of advanced structural and functional materials demands unprecedented combination of properties. This is to address the multifaceted and complex challenges of modern engineering and technology. These materials are expected to demonstrate extraordinary strength-to-weight ratios, enhanced durability, superior resilience in extreme environments, and complex property synergies (Fig. 1) for multifunctionality and adaptability [69]. Furthermore, the development of functional materials is oriented towards creating smart, responsive systems with capabilities such as self-healing, self-regulation, and property alteration on demand [70–74]. Additionally, there is a heightened focus on materials that can efficiently harvest, store, and transmit energy, alongside those capable of processing information at the nanoscale. Evidently, these advanced materials must align with sustainability imperatives, requiring attributes such as biodegradability, recyclability, or the potential for production from renewable resources [35,75–80]. Addressing these future material-property needs calls for a synergistic approach that integrates novel compositions, innovative processing methodologies, and precise control over material structure across multiple length scales [81–86]. This is to facilitate the realization of the intrinsic and extrinsic mechanisms driving the intricate array of desired properties.

Strength and ductility are critical mechanical properties that require synergistic applications in structural materials. Strength is the resistance of material to deformation which includes both yield strength (the stress at which a material begins to deform plastically) and ultimate tensile strength (the maximum stress a material can withstand before failure) [13,20–24,40,87]. Ductility, on the other hand, refers to the ability of the material to undergo plastic deformation before fracturing, allowing it to absorb energy under stress [88–92]. In conventional polycrystalline alloys, strength and ductility are often mutually exclusive [40]. Enhancing strength by refining microstructural features such as grain size often reduces ductility, potentially leading to sudden and catastrophic failure under mechanical load.

Nanocrystalline metals with grain sizes below 100 nm exhibit remarkable strength due to the Hall-Petch effect. However, these materials show significantly reduced ductility. This reduction in ductility becomes more pronounced as grain size decreases further, sometimes resulting in the inverse Hall-Petch effect, where the material becomes softer. This presents an ongoing challenge in materials science:

developing structural materials with no compromise of ductility for strength or vice versa. The uniform tensile strain before necking, a critical measure of ductility, is often reduced to just a few percent in these high-strength, fine-grained materials, compared to much higher ductility in their coarse-grained counterparts.

Complex concentrated alloys (CCAs) are alloys composed of multiple principal elements, typically in similar concentrations, whereas high entropy alloys (HEAs) are a subset of CCAs characterized specifically by high configurational entropy resulting from equiatomic or near-equiatomic proportions. The disruptive alloy design approach provides needed pathways for robust and synergistic structural and functional properties. For instance, strength-ductility synergy in CCAs/HEAs was introduced in 2004 [28] and is still in its infancy. The mechanisms driving this phenomenon are complex and multiple optimization challenge, involving the interplay of composition, processing complexities [13,20–28,33,41,87,93–102] phase stabilities [41,103–115] and deformation mechanisms [53,116–132]. Despite the growing interest, research focusing on the metallurgy and science of CCAs remains largely underdeveloped. Among the numerous and exponential research garnered in CCAs, innovative and novel pathways are being explored with unresolved issues and niche areas around heterogeneous microstructures [22,25,102,115,133–150], chemical heterogeneities [113,151–159] short-range order [126,156,160–168], interstitial alloying [151,169–177] and martensitic transformation-induced deformation [94–98,129–132,178]. Many of these research themes are targeted at mechanistic insights of strength–ductility synergy. Hence a consolidated and comprehensive assessment of the underlying mechanisms are warranted to underscore recent advances made, which is a justification for this review.

The purpose of this review is twofold. The first part presents a bibliometric analysis covering literature from 2014 to September 2024, addressing two key research questions: (1) What are the predominant research trends and thematic clusters in studies investigating strength–ductility synergy in CCAs/HEAs? and (2) How has the scientific literature evolved over the past decade regarding the mechanistic understanding of the strength–ductility synergy in CCAs/HEAs? The second part provides a consolidated critical assessment of recent mechanistic advances, specifically focusing on transition-metal-based CCAs/HEAs. Typical synergies between properties expected of advanced structural and functional alloys are shown schematically in Fig. 1 [69], showing hypothetical alloys A and B. Alloy A exhibits a superior balance of properties, meeting essential engineering criteria, including sufficient plastic strain, while Alloy B, despite excelling in some properties, fails to meet critical ductility requirements. Thus, Alloy A is better suited for practical engineering applications. Finally, the review highlights challenges, prospects, and future research directions to address material demands in modern structural applications.

2. Method and procedure

The strength-ductility synergy of complex concentrated metallic alloys was reviewed using peer-reviewed journal articles, conference proceedings, theses, dissertations, and research reports from various electronic databases. The articles considered are mainly in English. Keywords included “strength-ductility trade-offs”, “high strength and high ductility”, “complex concentrated alloys”, “high and medium entropy alloys”, “multi-principal element alloys”, and “microstructural and mechanical properties”. The retrieved articles were analysed bibliometrically (Fig. 2).

Bibliometric reviews, or science mapping, utilize text and data mining to analyse and visualize networks and correlations within research outputs [179–181]. This method mitigates the subjectivity found in narrative and systematic reviews [182]. For this study, Scopus was selected over Web of Science for its broader coverage of relevant articles [183]. Spanning 2014 to 2023, the study focused on publications containing the keywords “high entropy alloys,” “strength,” and “ductility,”

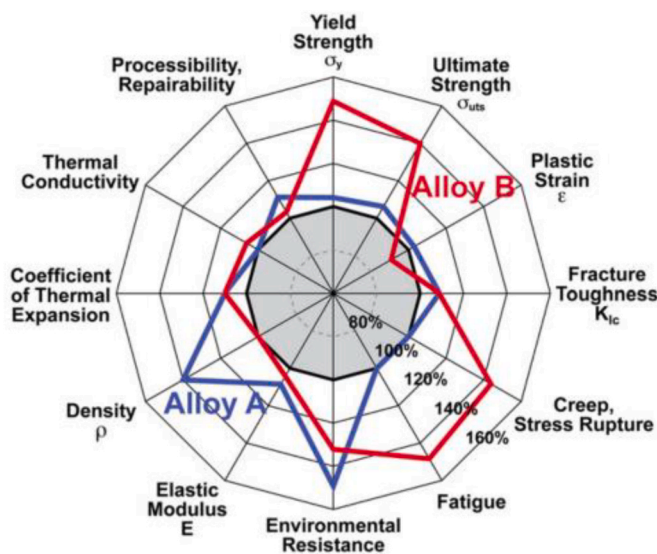


Fig. 1. Hypothetical alloys A and B that needs to fulfil fundamental properties to be able to compete with existing conventional grades schematically referred to as the grey polygon (Courtesy Elsevier and adapted from Ref. [69] with permission No. 6036351314342).

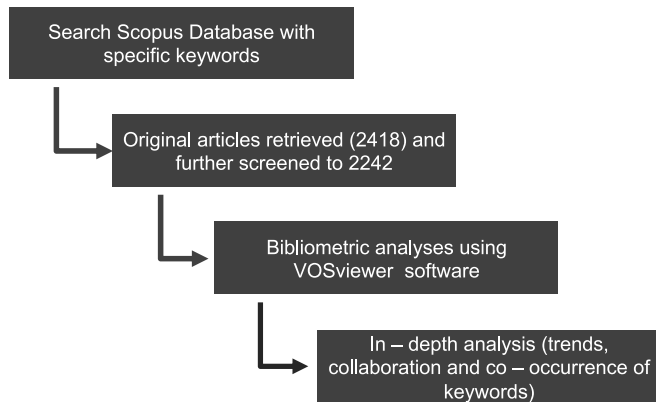


Fig. 2. Schematic flow chart of the bibliometric approach.

" yielding 401 pertinent articles after refinement from an initial 1010.

A schematic flow chart (Fig. 2) outlines the bibliometric analysis steps. Statistical and bibliometric analyses, including keyword co-occurrence, co-citation, and co-authorship networks, were conducted using VOSviewer. This software maps relationships between items (e.g., journals, authors, countries) based on proximity. The analyses revealed key research trends, influential publications, and collaboration patterns. A systematic review of significant findings and future research directions was also conducted.

3. Bibliometric assessment of strength-ductility synergy in CCAs

Key indicators of bibliometric assessment for strength-ductility synergy in CCAs are analysed. These mainly focused on research keywords, publication trends, distribution across journals, research areas, regional contributions, citation impact of influential papers, and limitations of current research with some identified niche areas for future exploration.

3.1. Publication trend of strength-ductility in HEA, from 2014 to January 2023

The interest in understanding strength-ductility synergy in HEAs/CCAs emerged in 2014. This was driven by the challenge of developing structural alloys with an appreciable balanced of properties, i.e., strength and ductility, which had an inverse relationship in dilute alloys [40]. It was hypothesized that relaxing solid solution strengthening in non-equiatomic compositions could optimize strength-ductility combinations [184–186]. It was suggested in 2016 that microstructural heterogeneities could favour strength-ductility synergy rather than the phase stabilization and single-phase formation [28,185]. Thus, the need to focus on prioritizing phase metastability and ductile multi-phase configurations.

The annual publication trend on strength-ductility combinations in HEAs from 2014 to September 2024 is discussed. The year-on-year distribution are given in Fig. 3. From 2014 to September 2024, over 2242 journal articles were published and indexed in Scopus. It comes with 9 publications in 2014 and then followed by steady annual growth until 2017. The publications in the area increased sharply from 2020 to 2024 with over 429 articles published from January to September 2024. Interest in strength-ductility synergy in CCAs/HEAs has steadily grown, with a 20–40 % annual increase in publications. A further 20–25 % rise is projected from September to December 2024 as shown by the shaded region in Fig. 3.

Building on the pioneering works in Refs. [28,184,185], interest in this area has grown significantly, as reflected in the rising number of annual and cumulative publications. Research has focused on various approaches [13,21–28,33,68,187–193] aimed at uncovering the mechanisms behind the strength–ductility synergy in CCAs. This surge is

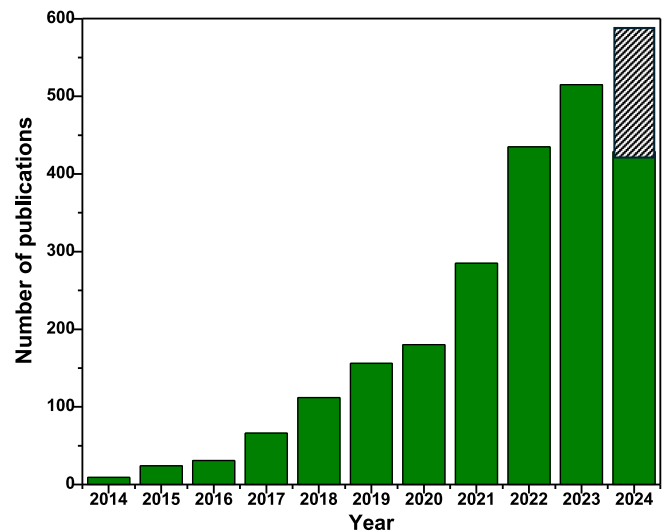


Fig. 3. Publications trend of HEA between 2014 and September 2024.

driven by the development of new alloy systems and detailed mechanical and microstructural characterization of established Cantor-based [194,195] and Senkov-based alloys [69,196–198]. As the design of CCAs/HEAs continues to expand, there is a growing need to identify potential engineering applications, motivating ongoing studies into their critical mechanical properties namely, strength and ductility.

3.2. Publications per research outlets

Table 1 highlights the top journals where manuscripts focusing on various aspects of the strength-ductility phenomena are published. It gives the total number of articles published and indexed in Scopus with the citations accrued from 2014 to September 2024. Knowing where authors publish and tracking their citations is important because it helps assess the quality, impact, and relevance of their research. High-impact journals with rigorous peer-review processes often signal that the work is credible and influential, while citation counts indicate how widely the research has been recognized and utilized by the academic community. This information is valuable for evaluating the expertise of the author, identifying key research areas, and making informed decisions in literature reviews, academic networking, and career advancement.

To access most contributions and citations, a threshold of at least 5 documents and 40 citations per journal was set. These criteria were selected to facilitate the analysis of the 2,242 publications, given the

Table 1

Bibliometric analysis of the top research journals publishing on the theme “strength-ductility” in CCAs.

S/ N	Journal	Number of articles	Citations
1	Materials Science and Engineering A	95	7336
2	Journal of Alloys and Compounds	65	1003
3	Acta Materialia	58	16292
4	Scripta Materialia	36	4038
5	Journal of Materials Science and Technology	34	2310
6	Intermetallics	21	2497
7	Materials and Design	21	2325
8	Materials Letters	16	1367
9	Scientific Reports	16	3265
10	International Journal of Plasticity	10	1335
11	Nature Communications	10	4611
12	Materials Characterization	10	1233
13	JOM	7	1359
14	Materials Research Letters	6	1091

lack of standardized criteria in the existing literature. The fourteen journals meeting these criteria are given in Table 1. Materials Science and Engineering A ranks first with the highest number of publications (95) and citations (7,336), underscoring its significance in HEA/CCA research on strength-ductility combinations. Journal of Alloys and Compounds follows with 65 publications and 1,003 citations. Despite fewer publications (58), Acta Materialia boasts more citations (16,292) than the combined total of the top two journals (8,339). Nature Communications, with only 10 publications, has more citations (4,611) than several other journals, highlighting the impact of journal reputation on citation rates, as noted in previous studies [199,200]. Generally, journals have higher citations and quality of publications due to factors such as rigorous peer-review processes, established reputations, and high impact factors, which attract top researchers and ensure that only significant, reliable research is published. Additionally, broad readership, accessibility, and effective promotion increase the visibility and citation of articles. Journals that focus on cutting-edge or interdisciplinary research often become key sources in their fields, further enhancing their citation rates and perceived quality.

3.3. Collaborative endeavours based on researchers, institutions and funding

Scientific collaboration is crucial for knowledge exchange, idea conceptualization, and access to research facilities [183]. It is also a key metric in ranking academic institutions and the quality of research being done. To generate the map illustrating scientific collaboration among researchers, the minimum thresholds were set at 5 documents and 10 citations per author. Out of the 1,207 authors in the database, 107 met these criteria and were grouped into 11 clusters (Fig. 4). The most prolific authors within these clusters include Wang H (cluster 1, red, 18

journals), Liaw PK and Liu Y (cluster 2, green, 16 journals), Wang J (cluster 3, blue, 23 journals), Mishra RS (cluster 4, yellow, 15 journals), Bhattacharjee PP (cluster 5, purple, 11 journals), Wang C and Xie Y (cluster 6, cyan, 9 journals), Zhang X (cluster 7, orange, 8 journals), Kim HS (cluster 8, dark brown, 8 journals), Zhang Y (cluster 9, light purple, 23 journals), Zhang Z (cluster 10, light red, 13 journals), and Li Z (cluster 11, light green, 20 journals). Journals within the same cluster exhibit higher co-citation rates. Additionally, larger nodes indicate greater influence or importance, based on the number of articles published or total citations received [201]. The shorter the line between two journals, the stronger their relationship [202].

The diversity of research collaboration and throughput is shaped by a complex interplay of factors, including substantial funding, institutional policies, and access to advanced facilities, which together foster multidisciplinary and international partnerships [183]. The presence of international postgraduate students and visiting scholars enhances cross-cultural exchange, while digital collaboration tools and open-access platforms further enable global research efforts, overcoming geographical constraints. These elements collectively drive diverse and productive collaborations across disciplines and borders.

Institutional co-authorship analysis (Table 2) was conducted using thresholds of ≥ 3 publications and ≥ 10 citations per institution. Out of 1,727 institutions analysed, 178 met the criteria. The top contributors include Northwestern Polytechnical University, Central South University, Pohang University of Science and Technology, Beijing Institute of Technology, and Yonsei University. Based on total link strength, Yonsei University (South Korea), Pohang University (South Korea), and Taiyuan University of Technology (China) lead in collaborative impact. Notably, the State Key Laboratory for Advanced Metals and Materials (China) stands out with 16 publications and 1,616 citations exceeding several institutions with higher output. Six of the top ten institutions are

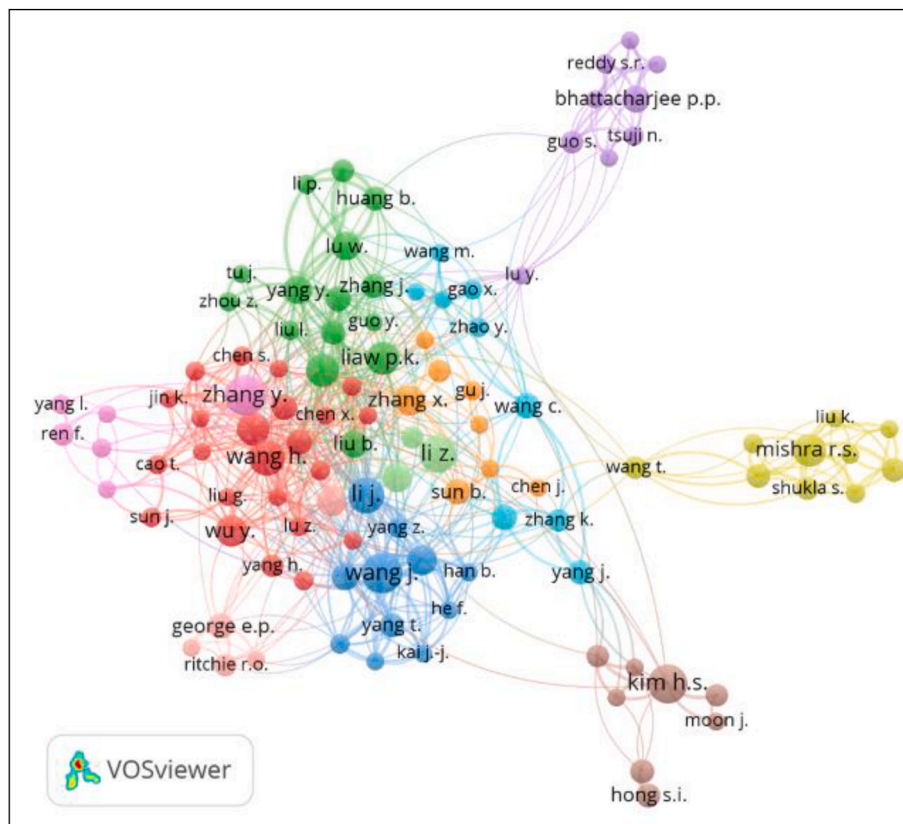


Fig. 4. Network map of the scientific collaboration between researchers in strength-ductility combination of HEAs are grouped into 11 clusters.

Table 2
Co-authorship analyses between the top ten institutions.

Rank	Institution	Total link strength	Documents	Citations
1	State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, China	14	28	1443
2	School of Materials Science and Engineering, Central South University, China	16	20	839
3	Department of Materials Science and Engineering, Pohang University of Science and Technology, South Korea	41	18	493
4	School of Materials Science and Engineering, Beijing Institute of Technology, China	17	18	418
5	Yonsei University (Institute for Convergence Research and Education in Advanced Technology), South Korea	44	18	278
6	University of Science and Technology (State Key Laboratory for Advanced Metals and Materials), China	9	16	1616
7	Dalian University of Technology (Key Laboratory of Solidification Control and Digital Preparation Technology), China	14	16	1391
8	University of Tennessee (Department of Materials Science and Engineering), Knoxville, United States	20	15	1261
9	Taiyuan University of Technology (Institute of Applied Mechanics, College of Mechanical and Vehicle Engineering), China	22	12	336
10	Oak Ridge National Laboratory (Materials Science and Technology Division), Oak Ridge, United States	14	10	1022

based in China, underscoring the high throughput and research intensity and leadership in the niche area of strength–ductility research focusing on CCAs/HEAs.

In addition to inter-institutional collaboration, international partnerships are crucial for advancing knowledge sharing and technology transfer. For the publication analysis by country in the study of strength–ductility in HEAs/CCAs, the criteria were set with a minimum of 5 documents and 10 citations per country. Fig. 5 shows the contributions of 48 countries, of which 23 meet these thresholds. Some countries overlap the same articles due to international co-authorship. In Fig. 5, node size represents the number of published articles, with China leading (623 publications, 21,876 citations, and 245 link strength), followed by the United States (139 publications, 16,620 citations, and 129 link strength) and South Korea (88 publications, 3,970 citations, and 66 link strength). Other notable contributors include Hong Kong, Japan, Germany (Cyan colour) and India.

3.4. Citations analysis of seminal articles on strength-ductility of CCAs

Based on the citation threshold of 100, ~28 seminal articles were identified as shown in Table 3. The most cited and seminal article was published in 2016 in Nature with 2,548 citations [28]. This was the pioneering study of strength–ductility synergy in CCAs/HEAs which explored the metastability of CCAs/HEAs. Among the 28 top-cited articles, eight were published in Acta Materialia, accumulating a total of 4,850 citations. Further details on these highly cited articles and their publication outlets are provided in Table 3. Another notable article demonstrated enhanced strength and ductility in a TiZrHfNb CCA through the addition of 2.0 at. % oxygen [204]. Additionally, an AlCoCrFeNi_{2.1} eutectic CCA achieved exceptional strength (1351 MPa) and ductility (15.4 %) due to uniform FCC(L12)/BCC(B2) lamellar microstructures [205], with cryo-milling and annealing further enhancing properties to 1437 ± 26 MPa and 14 ± 1 % [206]. These studies highlight that engineering composition, processing, and microstructure is key to achieving strength–ductility synergy in CCAs [28,204–211].

3.5. Keyword analyses focusing on strength-ductility of CCAs/HEAs

A co-occurrence analysis is a method used to visualize and map key concepts within a specific research field. This analysis helps authors

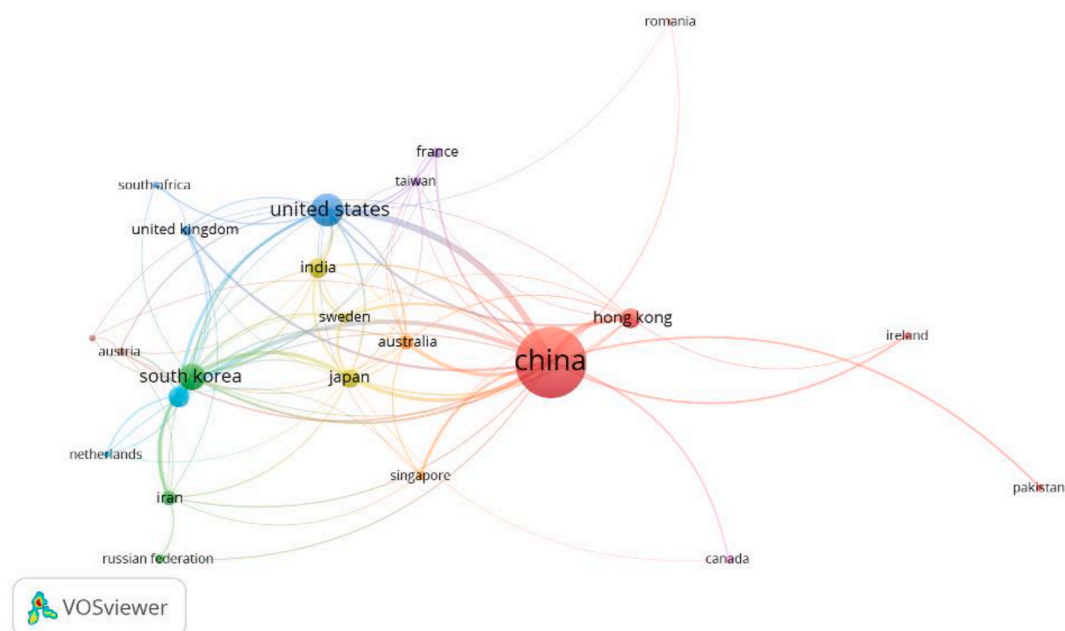


Fig. 5. Scientific collaboration network of countries on study of strength-ductility HEA.

Table 3

Topic articles with the highest citations and where it was published.

Article title	Journal	Citations
2016 – Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off [28]	Nature	2548
2016 – Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperature [10]	Nature Communications	1478
2016 – Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy [212]	Acta Materialia	1012
2018 – Enhanced strength and ductility in a high-entropy alloy via ordered oxygen complexes [204]	Nature	1257
2017 - Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi [213]	Acta Materialia	999
2017 – Heterogeneous precipitation behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy [214]		695
2019 – Enhanced strength–ductility synergy in ultrafine-grained eutectic high-entropy alloys by inheriting microstructural lamellae [215]	Nature Communications	676
2018 – Tunable stacking fault energies by tailoring local chemical order in CrCoNi medium-entropy alloys [216]	Proceedings of the National Academy of Sciences	637
2017 – Microstructural origins of high strength and high ductility in an AlCoCrFeNi _{2.1} eutectic high-entropy alloy [205]	Acta Materialia	612
2017 – A TRIP-assisted dual-phase high-entropy alloy: Grain size and phase fraction effects on deformation behavior [217]		599
2017 – Phase - Transformation Ductilization of Brittle High-Entropy Alloys via Metastability Engineering [209]	Advanced Materials	598
2017 – Dislocation mechanisms and 3D twin architectures generate exceptional strength-ductility-toughness combination in CrCoNi medium-entropy alloy [210]	Nature Communications	582
2019 – Ultrastrong Medium-Entropy Single-Phase Alloys Designed via Severe Lattice Distortion [218]	Advanced Materials	437
2019 – Tailoring heterogeneities in high-entropy alloys to promote strength–ductility synergy [219]	Nature Communications	411
2019 – Enhancement of strength-ductility trade-off in a high-entropy alloy through a heterogeneous structure [220]	Acta Materialia	388
2019 – Hierarchical microstructure design to tune the mechanical behavior of an interstitial TRIP-TWIP high-entropy alloy [211]		376
2016 – Ultrafine-grained AlCoCrFeNi _{2.1} eutectic high-entropy alloy [221]	Materials Research Letters	364
2017 – Strong and Ductile Non-equiatom High-Entropy Alloys: Design, Processing, Microstructure, and Mechanical Properties [222]	JOM	346
2016 – Precipitation behavior and its effects on tensile properties of FeCoNiCr high-entropy alloys [223]	Intermetallics	289
2018 – Simultaneous Strength-Ductility Enhancement of a Nano-Lamellar AlCoCrFeNi _{2.1} Eutectic High Entropy Alloy by Cryo-Rolling and Annealing [206]	Scientific Reports	254
2019 – Novel Co-rich high performance twinning-induced plasticity and	Scripta Materialia	238

Table 3 (continued)

Article title	Journal	Citations
transformation-induced plasticity high-entropy alloys [224]		
2019 – Simultaneously enhancing strength and ductility of a high-entropy alloy via gradient hierarchical microstructures [225]	International Journal of Plasticity	238
2019 – Probing the phase transformation and dislocation evolution in dual-phase high-entropy alloys [226]		233
2017 – Understanding the mechanical behaviour and the large strength/ductility differences between FCC and BCC Al ₄ CoCrFeNi high entropy alloys [227]	Journal of Alloys and Compounds	217
2017 – Effect of temperature on the fatigue-crack growth behavior of the high-entropy alloy CrMnFeCoNi [208]	Intermetallics	206
2017 – Precipitation strengthening of ductile Cr ₁₅ Fe ₂₀ Co ₃₅ Ni ₂₀ Mo ₁₀ alloys [228]	Scripta Materialia	201
2014 – Composition Dependence of Phase Stability, Deformation Mechanisms, and Mechanical Properties of the CoCrFeMnNi High-Entropy Alloy System [229]	JOM	191
2018 – Critical stress for twinning nucleation in CrCoNi-based medium and high entropy alloys [230]	Acta Materialia	169

identify critical research areas and knowledge gaps, while also providing insights into the interconnectivity between research topics and their associated methodologies. For the study of strength-ductility synergy in HEAs, a keyword occurrence threshold of 10 was set, with 36 out of 1444 keywords meeting this criterion. Fig. 6 shows the co-occurrence network, where node size represents the number of articles using each keyword, and line distance reflects the frequency of keyword co-occurrence. The 36 keywords are grouped into six clusters, with “high-entropy alloys” in green being the most prominent (442 occurrences, link strength of 706), followed by “mechanical properties” in red (243 occurrences, link strength of 469). The high-entropy alloys are mainly connected to other keywords such as complex concentrated alloys, deformation twins, heterogeneous structure, microstructure evolution, stacking faults, strength-ductility synergy, strengthening and tensile properties. Other significant keywords include “deformation mechanism” (light yellow, 42 occurrences, link strength of 77), “medium-entropy alloys” (blue cluster, 37 occurrences, link strength of 78), and “precipitation strengthening” (purple cluster, 35 occurrences, link strength of 70).

Further analysis highlighted keywords with the lowest link strengths, indicating underexplored areas. Keywords such as “refractory medium-entropy alloys,” “low cycle fatigue,” “TWIP,” and “precipitation behavior,” have the lowest link strengths of 3, suggesting they have not been extensively investigated by the scientific community. Additionally, synthesis methods such as powder metallurgy and spark plasma sintering have low link strengths, suggesting a research gap in these areas compared to more commonly used casting techniques for developing these alloys for strength-ductility synergy investigations.

3.6. Limitation of the bibliometric analysis

The keyword-based search was conducted primarily in English, leading to the exclusion of journals on strength-ductility published in other languages. This limitation affects the comprehensiveness of the research output, rendering the inferences and deductions from the literature largely qualitative. However, the data remains sufficiently quantitative to draw meaningful conclusions regarding the simultaneous enhancement of strength and ductility in structural CCAs.

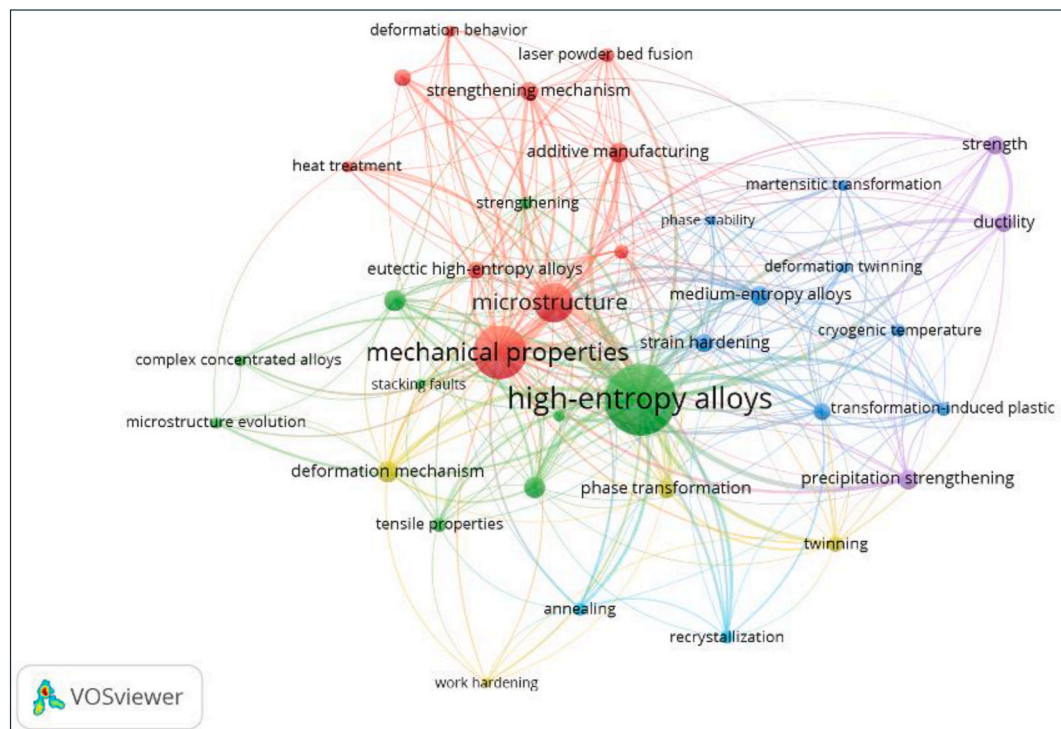


Fig. 6. Co-occurrence network of keywords based on occurrences.

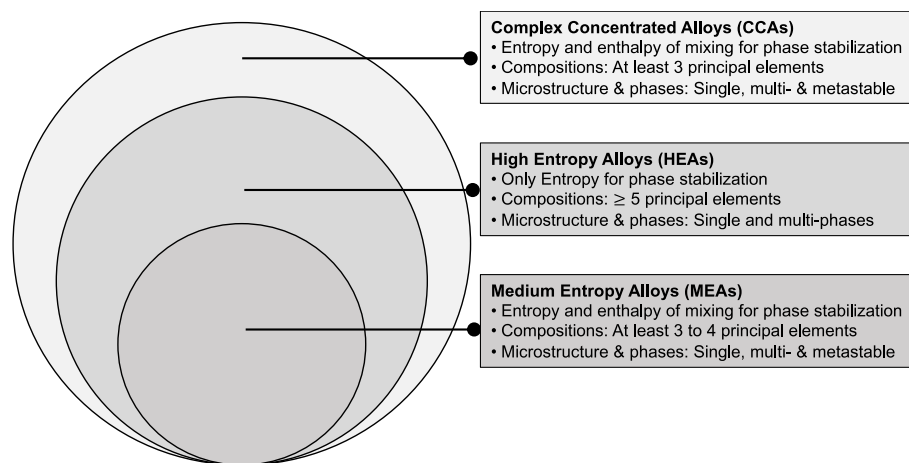


Fig. 7. Schematic diagram showing the classes of complex concentrated alloys based on compositions (Courtesy MDPI and adapted from Ref. [231] on Open access license).

4. Complex concentrated alloys and high entropy alloys

Alloy design has evolved towards compositionally complex alloys (CCAs), characterized by multiple principal elements without strict compositional constraints or a requirement to maximize entropy (Fig. 7) [231]. Their compositional versatility often produces multiphase microstructures, enabling tailored enhancements in properties such as strength and corrosion resistance. CCAs thus allow extensive exploration of compositional spaces to achieve diverse microstructural configurations and performance attributes.

High entropy alloys are considered the first generation of multiple principal element alloys with an entropic effect. The entropy-driven strategy in HEAs was initially intended to stabilize single-phase solid solutions (FCC, BCC, or HCP) and suppress the formation of

intermetallic compounds, thereby promoting homogeneous microstructures and well-balanced mechanical properties [232–239]. This principle of maximizing configurational entropy is central to achieving enhanced mechanical stability, strength, and corrosion resistance. However, as the development and exploration of diverse HEA systems expand, deviations from these original design assumptions are becoming more common [69,79,146,198,240–249]. Emerging studies increasingly highlight the potential of leaner compositions, previously overlooked, that can still deliver significant property synergies – challenging the early notion that only highly entropic, equimolar designs yield optimal performance.

The differences between CCAs and HEAs are multi-faceted. These are fundamentally around compositional ranges, the role of entropic contributions, phase formation, inherent design philosophy and property

Table 4
Fundamental differences between CCAs and HEAs.

Aspect	CCAs	HEAs
Definition	Multi-principal-element alloys (typically ≥ 3 elements) with no strict requirement for near-equi-molar ratios	A specialized subset of CCAs designed with near-equi-molar ratios (often ≥ 5 elements)
Compositional range	Wide variations in element concentrations; no need for balanced or near-balanced compositions	Nearly equimolar or close-to-equi-molar mixtures to maximize configurational entropy
Entropy contribution	Not necessarily driven by high configurational entropy; complex interactions among multiple elements are key	Intentionally high configurational entropy is central, fostering solid-solution phases
Phase formation	Can exhibit diverse and often complex phase structures, not solely determined by entropy	Typically forms simple solid solutions (FCC, BCC, or HCP) owing to high entropy
Design philosophy	Emphasizes tailoring of elements and structures for desired properties without a strict focus on configurational entropy maximization	Relies on entropy-driven stabilization as a core design principle
Property profile	Broad range of mechanical and chemical properties depending on composition and processing	Enhanced mechanical stability, strength, and corrosion resistance due to entropy effects

profile. These differences are highlighted in Table 4.

5. An overview of conventional strengthening mechanisms and models

An overview of the various traditional strengthening mechanisms is discussed. These are mainly solid solution, grain size/boundary, precipitation and dislocation strengthening mechanisms [131,250–253]. All these conventional strengthening mechanisms restrict dislocation movement increasing the yield and ultimate tensile strengths while reducing ductility considerably, as shown in Fig. 8 [178]. These have been explored for various CCAs/HEAs with the conventional strength-ductility trade-offs.

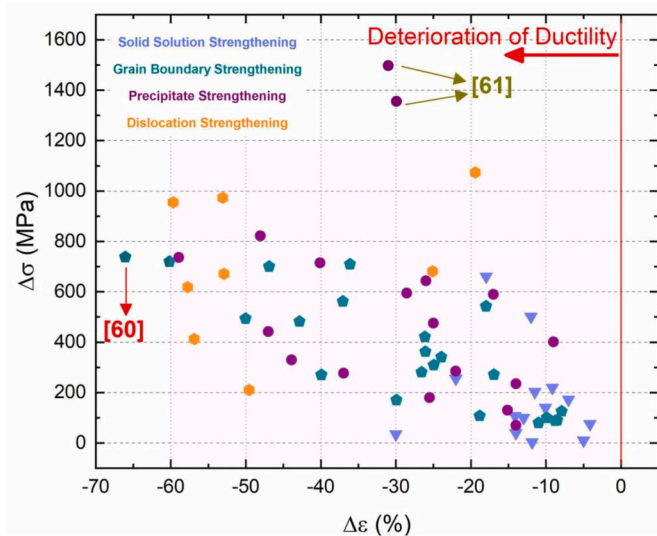


Fig. 8. Deterioration of ductility due to the contribution of the main traditional strengthening mechanisms such as solid solution, grain boundary, precipitate and dislocation strengthening mechanism (Courtesy Elsevier and adapted from Ref. [178] with permission No. 6046780625145).

5.1. Substitutional solid solution strengthening

Substitutional solid solution strengthening in CCAs/HEAs is achieved through a combination of interrelated interactions between constituent (solute/solvent) atoms and dislocations [254–260]. These are mainly elastic strain from atomic size differences (resulting in misfit) [162,218,261–264], modulus variations affecting strain fields [160, 265–267], stacking-fault energy reduction altering dislocation structure, electrical charge accumulation around dislocations, short-range atomic clustering creating slip barriers, and long-range order requiring dislocations to shear ordered regions [268–271]. These mechanisms work together in concentrated solid solutions like CoCrFeMnNi to impede dislocation motion, resulting in a desirable combination of high strength and ductility while maintaining a homogeneous, single-phase microstructure. Strengthening in substitutional solids arises from distortions and associated strain/stress fields, which are approximately 10 % of the shear modulus [254].

Based on solid solution strengthening models for FCC-based CCAs/HEAs, Equations (1)–(4) were used to describe various parameters were proposed [272,273]. Equation (1) provides the zero-temperature shear flow stress (τ_{y0}) as a function of the local misfit volumes arising from different atomic species, whereas Equation (2) is used to determine the activation-energy barrier (ΔE_b) that governs thermally activated dislocation motion [272]. Equation (3) then incorporates the effects of finite temperature and strain rate to calculate the shear yield stress, ($\tau_y(T, \dot{\epsilon})$), by reducing τ_{y0} through a thermal-activation term. Finally, the shear stresses are converted to the uniaxial yield strength in Equation (4) via a Taylor factor [272]. Thus, compositional fluctuations can be expressed through atomic-size misfits and elastic-modulus differences with effect on the flow stress at low and elevated temperatures, providing a powerful framework to predict strength in random solid-solution CCAs.

$$\tau_{y0} = 0.051\alpha^{\frac{1}{3}}\mu^{\frac{2}{3}}\left(\frac{1+\nu}{1-\nu}\right)^{\frac{4}{3}}f_{\tau}(w_c)\left[\frac{\sum_n C_n \Delta V_n^2}{b^6}\right]^{\frac{2}{3}} \quad (1)$$

$$\Delta E_b = 0.274\alpha^{\frac{1}{3}}\mu b^3\left(\frac{1+\nu}{1-\nu}\right)^{\frac{2}{3}}f_{\Delta E}(w_c)\left[\frac{\sum_n C_n \Delta V_n^2}{b^6}\right]^{\frac{2}{3}} \quad (2)$$

$$\tau_y(T, \dot{\epsilon}) = \tau_{y0}\left(1 - \left(\frac{kT}{\Delta E_b} \ln \frac{\dot{\epsilon}_0}{\dot{\epsilon}}\right)^{\frac{2}{3}}\right) \quad (3)$$

$$\sigma_y(T, \dot{\epsilon}) = 3.06\tau_y(T, \dot{\epsilon}) \quad (4)$$

Where: τ_{y0} is the zero-temperature flow shear stress, α is materials constant (~ 0.123 for typical calculations in CCAs/HEAs), μ is the shear modulus of the alloy, ν is the Poisson's ratio of the alloy, b is the Burgers vector magnitude of the dislocation, C_n is the molar (atomic) fraction of the n -th element, ΔV_n is misfit volume of the n -th species relative to the effective “matrix”, $f_{\tau}(w_c)$ and $f_{\Delta E}(w_c)$ are functions accounting for the dislocation bow-out geometry (mainly 0.35 and 5.7 respectively), T is absolute temperature, $\dot{\epsilon}$ is strain rate, $\dot{\epsilon}_0$ is the reference strain rate, k is the Boltzmann's constant, τ_y is the flow shear stress (shear) at temperature T and strain rate $\dot{\epsilon}$, σ_y is the uniaxial yield stress a function of Taylor factor (3.06 for an equiaxed FCC polycrystal).

5.2. Interstitial strengthening

Interstitial strengthening is a mechanism where small atoms in interstitial sites distort the lattice and hinder dislocation motion. The main examples of minute atoms are C, N, O, or B and their presence creates localized lattice distortions and strong elastic stress fields [109, 173,174,274–284], which interact with moving dislocations [285,286], raising the energy barrier for slip, thereby increasing strength. This mechanism is well-described in conventional alloys using classical

models of Fleischer [287,288] or Labusch [289]. However, the behavior in CCAs/HEAs is significantly more intricate as the solubility of these interstitials can be up to 5.5 at % [287]. The inherent chemical disorder and severe lattice distortion in these materials introduce complexities where interstitial effects are superimposed [151,169–172,177,290,291]. Interstitial atoms in CCAs/HEAs cause significantly greater lattice distortions than substitutional elements [292]. This complements the well-known strengthening from their multiple principal elements [232,241,293–298]. Hence, interstitial strengthening in CCAs/HEAs intensifies dislocation pinning and affect deformation mechanisms, cross-slip, twinning and modify stacking fault energies [169–172,282,283,290,299–304].

Interstitial atoms in CCAs/HEAs triggers various toughening and strengthening mechanisms. Addition of 0.5 at.% C into a non-equiatom, TRIP-assisted dual-phase Fe₅₀Mn₃₀Co₁₀Cr₁₀ CCA triggered the simultaneous activation of TWIP and TRIP mechanisms [245,292], owing to the carbon-induced tuning of the SFE to a critical threshold [175]. This resulted in strength – ductility synergy as shown in Fig. 9 [292]. Similarly, a 0.5 at.% C-doped CoCrFeMnNi enhanced the effect of strain hardening and strength upon twinning [305], whereas increased C to (~0.83 at.% showed the same trend in as-cast condition [306]. However, excessive carbon content (>1.7 at.%) leads to a significant reduction in ductility, highlighting the importance of compositional optimization and engineering the microstructural features from homogenous to inhomogeneous as shown in Fig. 10 for Fe₅₀Mn₃₀Co₁₀Cr₁₀, which is critical for strength – ductility synergy. These combined effects make interstitial crucial for fine-tuning the mechanical response of CCAs/HEAs across broad range of loading and environmental conditions [274,291].

Interstitial and substitutional solutes differ in position, size, and their effect on the host lattice. Interstitial atoms occupy spaces between lattice atoms and are much smaller, causing highly localized, anisotropic distortions [51], while substitutional atoms replace host atoms and induce more uniform strain [306–309]. Interstitials interact more strongly and directionally with edge dislocations and form Cottrell atmospheres that effectively pin dislocations [310]. In contrast, substitutional strengthening arises mainly from size and modulus mismatch [160] [160,162,261,262,266,267,311]. Additionally, interstitials diffuse much faster, influencing dynamic strain aging and creep. These factors make interstitial strengthening especially effective in BCC-based CCAs/HEAs [173,278–280,307].

Interstitials can significantly enhance yield strength ($\Delta\sigma_y$) in FCC alloys, as shown in Table 5. For instance, nitrogen strengthens austenitic stainless steels by solid solution hardening and increasing the work hardening rate, though its mechanism remains not fully understood. Even greater strengthening is observed in ordered FCC (L1₂) alloys,

where additions like B yield lattice resistance increases of 400–900 MPa/at%. Overall, interstitials provide a much higher $\Delta\sigma_y/\Delta c$ than substitutional elements.

5.3. Grain size/boundary strengthening

Grain size/boundary strengthening enhances the mechanical properties of CCAs/HEAs. The two proposed models are the dislocation pile-up and work hardening models. The dislocation pile-up model is associated with the interaction of line defect (dislocations) with grain boundaries hindering dislocation motion resulting in pile-ups [268–271]. This results in local stress concentration which makes it possible for the propagation of plastic deformation through the grain boundary. The mechanism of propagation of deformation is by the operation of dislocation sources in the neighbouring grain or the emission of dislocation from grain boundary ledges [268,270,271]. These theories yield an inverse square root grain size dependence of the yield stress and the flow stress. In this model the controlling factor is the stress required to generate dislocations. In the Hall-Petch-Cottrell dislocation pile-up model, the grain boundaries act as strong barriers to dislocation motion and the formation of grain boundary dislocation pileups leads to pronounced stress concentration localized at the grain boundary [268,320]. However, the limitation of the model is its inability to account for the effects of interstitial elements that could occur the octahedral and tetrahedral sites with pronounced effects on the yield strength, especially in structural steels. These dislocations which are line defects are drivers of plastic deformation [112,321–323,325]. Grain boundaries, the interfaces between individual crystals (grains) within a material, act as obstacles to dislocation motion. These boundaries disrupt the regular atomic arrangement, causing dislocations to pile up at the boundary, change their slip direction, or require higher stress to propagate across. This increases the yield strength of CCAs/HEAs, and other auxiliary mechanisms are stacking fault slip mechanism in AlCoCrFeNi [325], Hall – Petch effects in CoCrFeNi and CoCrFeMnNi [326–328] and the segregation of secondary phase at the grain boundary in FeCoCrNi alloys [328–331].

The relationship between grain boundary strengthening and the Hall-Petch effect is explicitly defined by the Hall-Petch effect in Equation (5) (Hall, 1951a) [58]. This equation demonstrates that the yield strength of a material increases proportionally to the inverse square root of its mean grain diameter [62,66,112,322,323,332,333]. In CCAs/HEAs, which often exhibit sluggish diffusion kinetics and the potential for fine-grained microstructures, the Hall-Petch effect plays a crucial role in tailoring their mechanical properties [112,321–325]. By controlling processing parameters to achieve finer grain sizes, the strength of HEAs/CCAs can be significantly enhanced, often in conjunction with

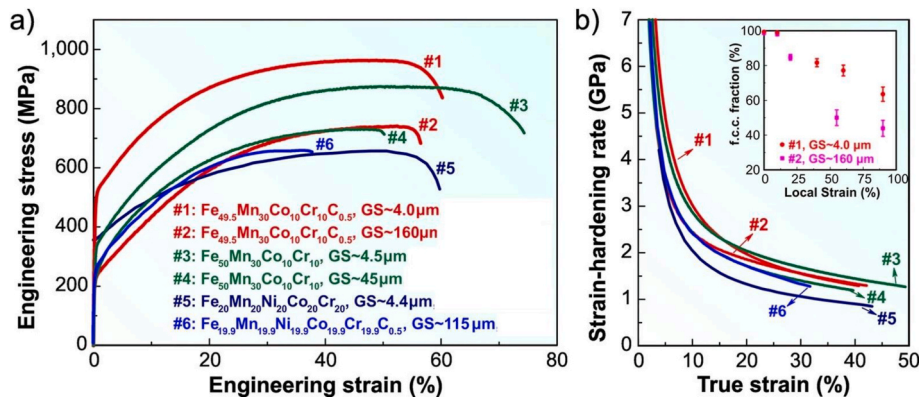


Fig. 9. Mechanical behaviour of interstitial FeMnCoCr showing (a) stress strain and (b) working hardening resulting in property synergy (Courtesy of Nature, adapted from Ref. [292] under Open Access License).

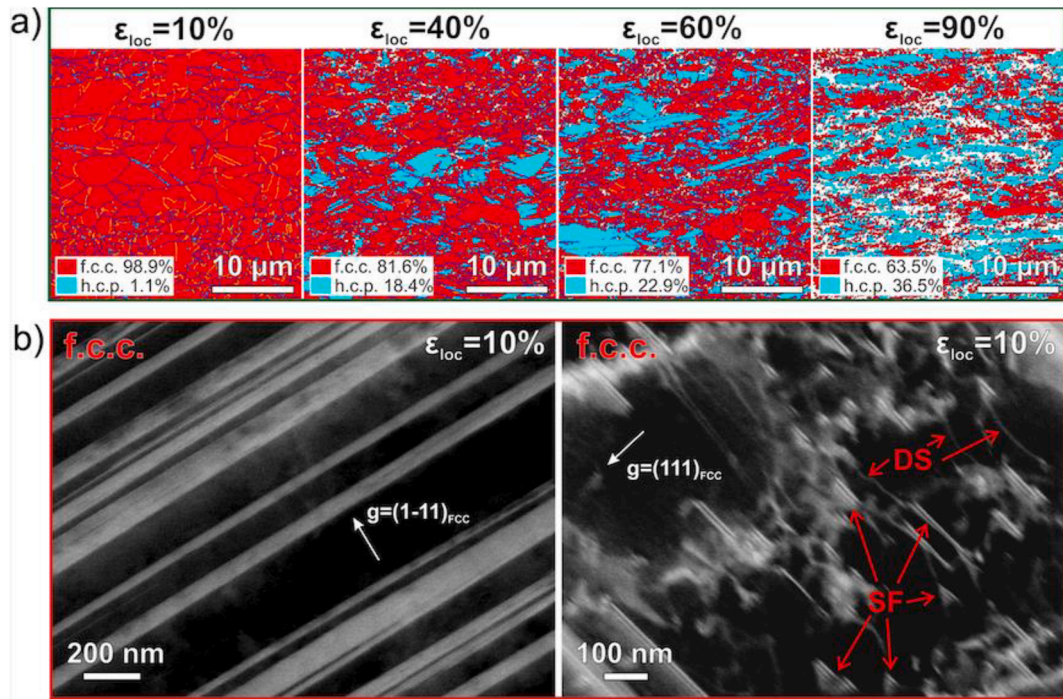


Fig. 10. Microstructure of Fe50Mn30Co10Cr10 CCA with (a) EBSD phase maps with the deformation-induced martensitic transformation at different local strain levels of 10 %, 40, 60 and 90 % corresponding to early, medium, late uniform deformation and post-necking stages and (b) electron channelling contrast image (ECCI) showing deformation twins, stacking fault (SF) and dislocations (DS) in the FCC phase (Open access and adapted from Ref. [292]).

Table 5

The ratio of change in yield strength and concentration ($\Delta\sigma/\Delta c$) of interstitial C and N in FCC alloys at room temperature.

Alloy	Interstitial	$\Delta\sigma/\Delta c$ (MPa/at%)	Ref
CrCoNi	C	140	[312]
Fe40.4Ni11.3Mn34.8Al7.5Cr6		184	[313]
CoCr0.25FeMnNi		64	[314]
TWIP steels		26 – 62	[315]
CoCrFeMnNi	C and N	117 – 120	[305,316]
316 stainless steel	N	110	[317]
Fe – 18Cr – 10Ni		180	
Cr15Fe46Mn17Ni22		95	[318]
Fe – 19Cr – 10Ni		125	[285]
Fe – 18Cr – 14Ni – 3Mo		80	[319]

their inherent solid solution strengthening effects [334–338]. The ability to manipulate both composition and grain size provides a powerful approach to optimize the strength-ductility balance in these advanced metallic materials [23,87,91,115,327,339–343]. A similar Hall-Petch relation does apply to flow stresses as shown in Equation (6). The widely accepted inverse square root dependence of yield strength on grain size has been challenged for coarse-grained materials, where yield strength may scale with the inverse of grain size. However, this relationship is not conclusively established – flow stress plotted against $1/d^n$ often shows minimal deviation from linearity for n values between 1/3 and 1.

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad (5)$$

where σ_y is the yield strength, σ_0 is the friction stress (resistance to dislocation motion within the grains), k_y is the grain boundary strengthening coefficient, and d is the average grain size.

$$\sigma_F(\varepsilon, d) = \sigma_0(\varepsilon) + \frac{k_F(\varepsilon)}{\sqrt{d}} \quad (6)$$

The work hardening model is associated with uniform straining of the polycrystalline materials. Once there is straining, the tendency for volume defects such as voids to be nucleated at some grain boundaries is high with the possibility of having some grains to overlap. This introduces the geometrically necessary and statistically stored dislocations [81]. The formation of the GNDs is due to the accommodation of the strain incompatibility between the grains resulting from the difference in crystallographic orientation [344–347]. This is critical to the work hardening model, where the smaller the grain sizes, the higher the rate of dislocation accumulations.

The finer the grain size, the greater the total area of grain boundaries within the material, leading to more effective obstruction of dislocation movement and consequently higher strength [134,348–358]. This strengthening mechanism is particularly significant in polycrystalline materials where grain size can be controlled through processing techniques. The strength against percentage total elongation for various CCAs/HEAs with varying grain sizes, mainly nanocrystalline, ultrafine-grained, and coarse-grained is given in Fig. 11 [95]. The data mainly cluster in an inverse relationship between strength and ductility, forming a broad “banana-shaped” region. Alloys with nanocrystalline or ultrafine grains show high UTS with limited elongation, reflecting enhanced grain boundary strengthening at the expense of ductility. As grain size increases, the UTS decreased with relatively high elongation showing the classic strength – ductility trade-off [67,152,170,328,359]. By exploring the composition-processing-structure behaviour of CCAs/HEAs, grain sizes can be engineered to induce the Hall – Petch effects. Although, grain refinement can drastically increase strength, compositions and thermal-mechanical treatments can be tailored for strength – ductility synergy [95].

5.4. Dislocation strengthening

Dislocation strengthening in HEAs/CCAs arises from the accumulation and interaction of dislocations, increasing flow stress. Severe lattice distortion and compositional fluctuations in these alloys amplify these interactions, leading to enhanced hardening beyond conventional dilute

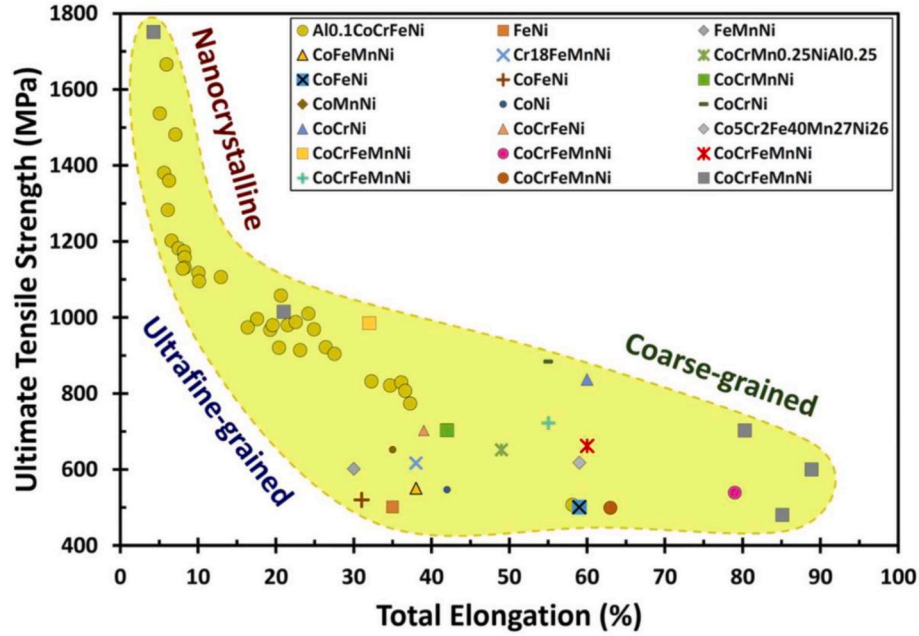


Fig. 11. Grain size effect on strength – ductility of CCAs/HEAs (courtesy Elsevier and adapted from Ref. [95] with permission No. 6036700898095).

alloys. Generally, dislocation density is proportional to the yield strength and is quantified by the Bailey-Hirsch relation (Equation (7)).

$$\Delta\sigma_D = M\alpha Gb\sqrt{\rho} \quad (7)$$

where $\rho = \frac{2\sqrt{3}\epsilon}{Db}$

5.5. Precipitation strengthening

Precipitation strengthening is a process where there is lattice discontinuity introduced in the microstructure. The discontinuity is attributed to high volume fraction of precipitates which provide strong obstacles to dislocation glide [360–367]. In general, large and hard incoherent precipitates are bypassed by dislocations leaving dislocation loops, whereas small and soft coherent precipitates are cut through by passing dislocations. The strengthening mechanism due to precipitation cutting is given as $(\sqrt{f} \times r_p)$ where r_p is precipitate particle radius and “f” as the volume fraction [368–370]. The main precipitation cutting mechanisms are coherency hardening ($\Delta\sigma_C$) (Equation (8)), chemical hardening, modulus hardening ($\Delta\sigma_M$) (Equation (9)) and order hardening ($\Delta\sigma_0$) (Equation (10)) [371]. The precipitation bypassing mechanisms due to the hard and large precipitates, which are too strong and not easily sheared by the dislocations have the strengthening proportional to $\sqrt{f}/r_p$ [368–372]. This is known as the Orowan dislocation bypass mechanism. In (CoCrNi)94Ti3Al3 alloy [371], the coherent precipitates were of the L1₂-types, whereas the incoherent ones are

mainly σ -types, which has direct effects on the yield strength [360,361, 371]. These summarized for some CCAs in Table 6.

$$\Delta\sigma_C = M\alpha_c (G\epsilon)^{3/2} \sqrt{\left(\frac{rf}{0.5Gb}\right)} \quad (8)$$

$$\Delta\sigma_M = 0.0055M(\Delta G)^{3/2} \left(\frac{2f}{G}\right)^{1/2} \left(\frac{r}{b}\right)^{\frac{3m}{2}-1} \quad (9)$$

$$\Delta\sigma_0 = 0.08M \frac{\gamma_{APB}}{2b} \sqrt{\left(\frac{3\pi f}{8}\right)} \quad (10)$$

The impact of coherent and incoherent precipitates on mechanical properties is pronounced. In terms of yield and ultimate tensile strengths, the coherent precipitates in CCAs/HEAs provide the needed pathway for better strength – ductility synergy compared to the incoherent precipitates [377]. This is due to capacity of coherent precipitates hindering dislocation motion while maintaining lattice continuity that leads to enhanced work hardening and delayed fracture. Some of the coherent precipitates are L1₂ type Ni₃Ti nanoclusters observed in FeCoNi [378], CoCrFeNi [379] and other CCA systems [380–382,397]. The incoherent precipitates contribute to high strength with compromised ductility as they act as stress concentration points and sites pronounced for early crack initiation.

Metal additive manufacturing (MAM) addresses the limitations of conventional CCA/HEA fabrication. This is enabled by complex geometries, design flexibility, and mass customization, while improving material, energy, and time efficiency [383]. It also allows for deliberate microstructural heterogeneity with controlled precipitates [384], exhibiting coarse columnar grains and a supersaturated, dislocation-rich matrix [378,385–388], promoting enhanced strength and toughness simultaneously. Thus, precipitates contribute significantly to improved mechanical properties for additively manufactured CCAs.

Table 6

Families of CCAs/HEA with coherent precipitates contributing to strength – ductility synergy.

Alloy system	Precipitates	σ_y (MPa)	σ_{UTS} (MPa)	Elongation (%)	Ref
Al _{0.2} Co _{1.5} CrFeNi _{1.5} Ti _{0.3}	∅	781	1042	20.58	[373]
	L1 ₂ + L2 ₁	1235	1550	10.69	
Ni _{2.1} CoCrFeNb _{0.2}	∅	340	735	43	[374]
	γ	897	1127	17	
FeCoCrNiC _{0.05}	∅	708	872	14.5	[375]
	Cr ₂₃ C ₆	787	950	10.3	
AlCoCrFeNi	FCC	1170	2940	21.6	[376]

6. Mechanistic insights of strength-ductility synergy in CCAs/HEAs

Complex concentrated alloys represent a novel class of materials that challenge traditional alloy design principles. This is by incorporating

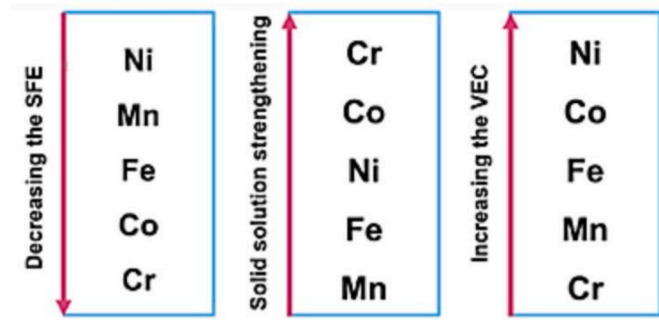


Fig. 12. Effects of alloying elements on SFE, solid solution and VEC of the Cantor alloy (Courtesy Elsevier and adapted from Ref. [101] with permission No. 6036740018407).

multiple principal elements in near-equiatomic concentrations [195, 241, 389]. This unconventional composition results in a unique combination of properties, including high strength, enhanced ductility, and exceptional resistance to wear, corrosion, and high-temperature environments [13, 20–24, 41, 68, 93, 178, 187, 390]. The design philosophy behind CCAs/HEAs focuses on exploring vast compositional spaces to uncover new phases and microstructures driven by the high configurational entropy and enthalpy of mixing [336, 391–395]. This broadens the range of material properties enabling the development of materials tailored for specific, demanding applications.

Many CCAs/HEAs exhibit an excellent strength–ductility balance from a compositional standpoint. These include both equiatomic and non-equiatomic compositions, as well as alloys incorporating metalloids such as Si [93] and Ge [95]. For the equiatomic Cantor (CoCrFeMnNi) alloy, Fig. 12 details how its constituent elements influence SFE, solid solution strengthening, and VEC. When Cr exceeds 20 at% in CoCrFe–NiMn, it lowers SFE [379, 396], yet promotes sigma phase formation, undermining ductility [252, 398]. Meanwhile, Co increases solid solution strengthening and further reduces SFE [397, 399] and raising its content can suppress sigma formation by elevating the VEC [400]. In contrast, adding Fe and Mn beyond equiatomic levels do not strengthen [399] nor prevents Cr-, Fe-, and Mn-driven sigma phase generation [401].

The mechanisms driving the strength–ductility synergy in CCAs/HEAs are multifaceted. These involve an interplay of compositional complexities, microstructural characteristics, phase stabilities and deformation mechanisms [20, 41, 68, 93, 178, 187, 390, 402, 403]. These alloys, characterized by their multi-element compositions, exhibit

unique structural and functional properties that arise from the complex microstructures and the interactions between various alloying elements. This is what is generally termed the cocktail effects [133, 404]. The main mechanisms are maximization of configurational entropy and enthalpy of mixing [9–11, 233, 234, 240, 405–407], microstructural heterostructural tailoring [408–414], twinning and transformation induced plasticity [16, 47, 108, 300, 415–421], back stress strengthening [422–424], nanoscale precipitation [21, 23, 25, 26, 153, 187, 192, 193, 203, 425], controlled processing techniques [33, 189, 191, 203, 426–431] and conventional multiple strain hardening and grain size refinement. Understanding these mechanisms is crucial for the development of robust structural and functional materials for demanding applications without compromising fundamental and critical properties.

The strength–ductility synergy in CCAs/HEAs is inherent in the combination of the crystal structures and phase compositions. This is shown in Fig. 13 where the yield and ultimate tensile strengths with elongation to fracture of various CCAs/HEAs with different crystal structures (FCC, BCC) and phase compositions (single-phase, dual-phase, and multi-phase) are compared [432]. In Fig. 13(a), yield strength is plotted against elongation, whereas in Fig. 13(b) ultimate tensile strength is shown against elongation. The FCC CCAs/HEAs generally have high ductility with moderate to high strengths, whereas BCC CCAs/HEAs show the reverse [432]. However, multi-phase alloys (dual or more than two phases) provide good spread indicating how combining different phases, strengthening and toughening mechanisms can promote strength and ductility synergy [95, 99, 360–362, 371, 433–435]. These relationships underline the versatility of HEAs and highlight the importance of crystal structure and phase constituents in tailoring mechanical properties.

6.1. Maximization of configurational entropy and enthalpy of mixing

Maximization of configurational entropy and enthalpy of mixing is a rudimentary concept in the design of CCAs/HEAs. It is one of the five core effects referring to the randomness of the atomic arrangements in CCAs due to the multiple principal elements in equiatomic or near-equiatomic amounts [1, 9, 10, 12, 24, 236–239, 242, 405, 436–442]. The maximized configuration entropy is estimated to be higher than $1.5R$ (R – the gas constant) [194, 195, 232, 443–446] and determined from the Boltzmann statistical relation [397]. It addresses the thermodynamics of CCAs/HEAs. This stabilizes the crucial solid solution phases and other microstructural features that contribute to the overall structural and functional properties of CCAs such as strength and ductility [103, 104, 184, 185, 406, 407, 447–449]. The phenomenon is observed for across the various families of CCAs. The effects benefit from the complex chemical

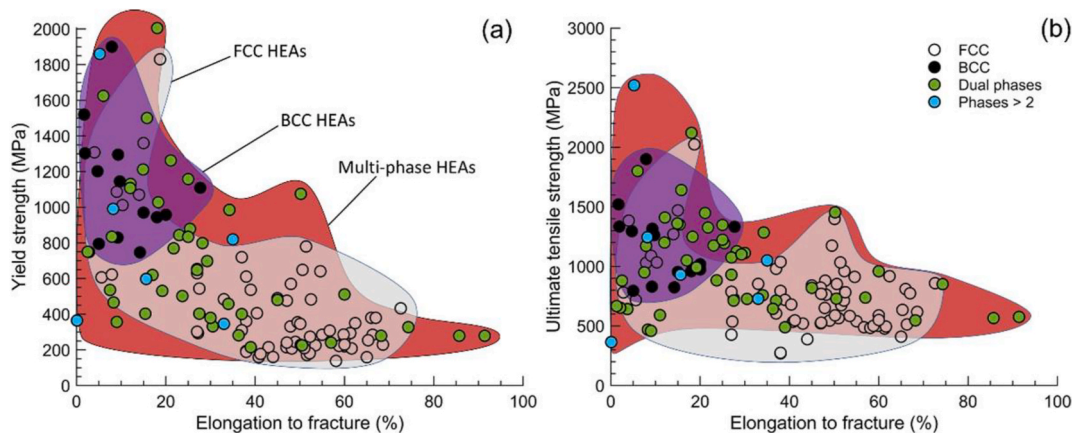


Fig. 13. Trends of the strengths to elongation behaviour of CCAs/HEAs as a function of crystal structures and phase compositions with (a) yield strength and (b) UTS with elongation to fracture [432].

heterogeneities affecting the stacking fault energy [151,152,450], which is mostly not prevalent in dilute alloys.

The contribution of this phenomenon to strength – ductility synergy is in the stabilization of the solid solution phases [234,451–454]. High configuration entropy stabilizes the single-phase solid solutions over other intermetallics, inclusions and precipitates, promoting high strength without compromising ductility [119,123,185,203,453–455]. This reduces the tendency for phase separation which aids in the distribution of stress, leading to improved strength. The enthalpy of mixing reflects the interactions between different elements contributing to the formation of unique microstructures with varying degrees of lattice distortion and local bonding variations [41,178,242,456]. These microstructural features enhance dislocation interactions and work hardening rates, allowing CCAs to achieve a superior balance of strength and ductility. This has been observed in most Cantor-derived 3D transition metals such as CrCoNi, VCoNi, CrCoFeMnNi. In CrCoFeMnNi, the effects are associated mostly with the solid solution FCC structure resulting in exceptional properties including high strength and high ductility [9,10,459].

The random distribution and interaction of the different alloying elements in near-equiatomic composition leads to chemical heterogeneities with complex energy landscape [151,455–458,460]. This has direct effects on increased dislocation mobility which is effective for plastic deformation [461]. This contributes significantly to improving ductility in the alloy while ensuring no compromise in strength and hardness. Furthermore, the random interaction of constituent elements exhibits reduced susceptibility to embrittlement mechanisms. A typical example is hydrogen embrittlement. In dilute alloys, hydrogen atoms diffuse into the microstructure of the metal, interacting with grain boundaries, dislocations, and precipitates [462–465]. These hydrogen atoms accumulate at grain boundaries, reducing the cohesive strength between grains and making the material more susceptible to intergranular fracture and compromised ductility. This has been reported for specialty alloys such as Inconel 718 and AISI 310 (Fig. 14) [466]. Additionally, hydrogen atoms interact with dislocations, creating

hydrogen-dislocation complexes that impede dislocation movement, leading to localized stress concentrations and crack initiation. In the presence of precipitates or second-phase particles, hydrogen can cause decohesion at the matrix-precipitate interface, further promoting crack propagation. These interactions weaken the overall structure of the alloy, leading to a reduction in ductility and toughness, and resulting in embrittlement. The combined effect of these microstructural interactions can severely compromise the mechanical performance, particularly under tensile stress or cyclic loading conditions [462–465, 467,468].

The unique multi-element composition of CCAs creates a high degree of lattice distortion and a complex energy landscape, which can inhibit the formation and mobility of harmful hydrogen-induced defects such as hydrides or brittle phases commonly seen in dilute alloys [303,466,469, 470]. Instead of causing embrittlement, hydrogen in CCAs can stabilize certain microstructural features, such as dislocations or twin boundaries, that contribute to work hardening (Fig. 14(c)). This stabilization can lead to a more uniform distribution of stress and strain, improving ductility. Furthermore, the increased resistance to hydrogen-induced cracking in CCAs allows for higher stress thresholds, resulting in enhanced strength [466]. Thus, interaction of hydrogen with the complex microstructure of CCAs leads to a synergistic improvement in both strength and ductility [466]. This has mainly been attributed to the maximization of configurational entropy and enthalpy of mixing of near-equiatomic composition with the local chemical ordering [110, 162,169,461,471,472].

The hydrogen mechanism contributing to strength-ductility synergy in metals are multifaceted. These involve several interrelated phenomena but primarily underpinned by hydrogen-enhanced local plasticity (HELP) [310,473–475] and hydrogen-induced nano-twinning [48,349, 466,476,477]. Hydrogen facilitates dislocation mobility by reducing barriers [48,310,474,475,478], enabling more homogeneous deformation, and promoting extensive strain hardening. Concurrently, hydrogen encourages deformation twinning at lower stress levels [462–465,467, 468], creating a refined microstructure with enhanced grain-boundary

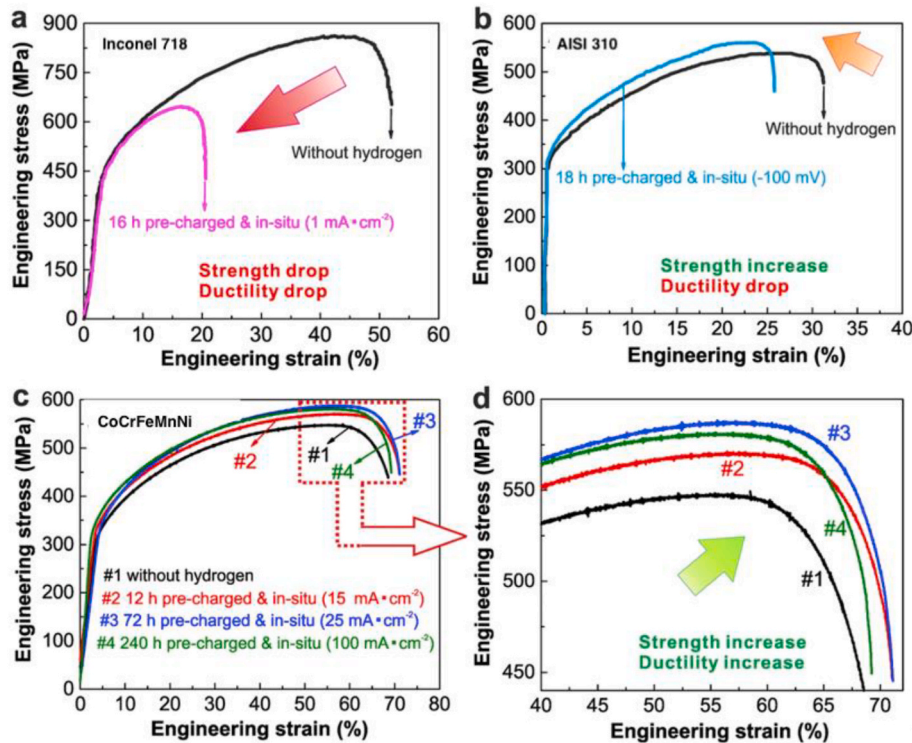


Fig. 14. Effect of hydrogen charging on stress-strain curves of selected dilute and complex concentrated alloys of (a) Inconel 718, (b) AISI 310, (c) CoCrFeMnNi with (d) showing the simultaneous increasing of strength and ductility at high magnification [466].

strength. These combined effects prevent premature localization of strain [48,310,349,466,473,475,477], delaying necking and fracture initiation, which leads to improved ductility and toughness alongside increased strength.

Hydrogen stabilizes metastable phases such as austenite in steels. This delays transformation into brittle phases during deformation [276, 294,479,480]. This metastability contributes to sustained, uniform plastic deformation and increased strain-hardening capacity [37,466, 479,481], simultaneously enhancing strength and ductility. When precisely controlled, hydrogen modifies grain boundary behaviors positively, strengthening grain boundaries and reducing susceptibility to intergranular fracture. Thus, under controlled conditions, hydrogen transitions from an embrittling element to a beneficial component that significantly improves both mechanical strength and ductility in metallic alloys [48,310,349,466,473,475,477].

High configurational entropy and enthalpy of mixing provide pathways for improved damage tolerance and easily tailored for improved mechanical properties. This leads to combined effects of intrinsic and extrinsic toughening mechanisms which improve damage tolerance [482–484], thus strength – ductility synergy. This has been observed in CrCoFeMnNi 442 and TiZrHfNbTa [485,486]. Furthermore, by maximizing the configuration entropy and enthalpy of mixing, structural properties of CCAs are improved. The AlCoCrFeMo with high entropy of $\sim 1.61R$ (R = gas constant) has remarkable stabilization of the solid solution and the matrix phases [379]. This contributed to the strength – ductility synergy.

6.2. Negative enthalpy of mixing of solid solutions

Negative mixing enthalpy reflects the energy decrease when different atoms combine in an alloy, indicating strong chemical affinity between elements and favourable atomic bonding. This enhances structural stability, and in CCAs, it promotes chemical heterogeneities like local fluctuations or short-range order [482,487]. These heterogeneities impede dislocation motion, improving strain hardening, which is essential for achieving high strength and ductility. Key factors influencing negative mixing enthalpy include elemental interactions (chemical ordering and pair interactions) [482–484], configurational entropy [234], complex formation [488] and ionic radius of constituent

elements [488].

Adding elements like Al and Ti, which have a strong ordering tendency, to a base alloy such as CoFeNi can lead to localized short-range ordering (SRO) or long-range ordered (LRO) domains due to their negative mixing enthalpy with Co, Fe, and Ni. This ordering effect increases the tensile yield strength from around 181 MPa in CoFeNi to ~ 793 MPa in AlTiCoFeNi [482]. In the HfNbTiVAl10, the addition of Al resulted in negative mixing enthalpy that strengthens atomic bonding and drives chemical segregation [487]. This leads to the formation of numerous heterointerfaces, acting as barriers to dislocation motion and boosting strength. Simultaneously, these chemical fluctuations enable varied dislocation behavior, allowing the alloy to sustain plastic deformation and delaying plastic instability [487], resulting in exceptional tensile ductility and strength, breaking the traditional strength-ductility trade-off in CCAs.

Similarly, negative enthalpy of mixing was used to guide the design of FeCoNiAlNbB for strength – ductility synergy. Elements with large negative mixing enthalpies such as Al and Nb with Fe, Co, and Ni were selected to induce strong chemical interactions [489], promoting the formation of ordered $L1_2$ nanoprecipitates within a ductile FCC matrix. These nanoprecipitates significantly enhance strength through ordered precipitation strengthening, while maintaining coherency and nano-scale size to limit their obstruction of dislocation motion and magnetic domain wall mobility. This balance preserves high ductility and low coercivity. Thus, negative mixing enthalpy is key to microstructural optimization for superior mechanical properties and performance.

6.3. Contribution of dominant mechanisms to strength-ductility in CCAs

A critical focus in CCAs/HEAs research is achieving strength-ductility synergy to overcome the traditional trade-off between these mechanical properties. The compositional complexity and multi-principal element structures of these alloys offer a promising platform for simultaneously enhancing strength and ductility [41,93,178,390, 402,490] – features often mutually exclusive in conventional alloys [40]. This pursuit is crucial for meeting the rigorous demands of next generation structural and functional applications [119,184,185,203, 246,294,436,491,492]. Fig. 15 shows the synergy in an interstitial TWIP-TRIP CCA, which outperforms traditional alloys like steels, Ti,

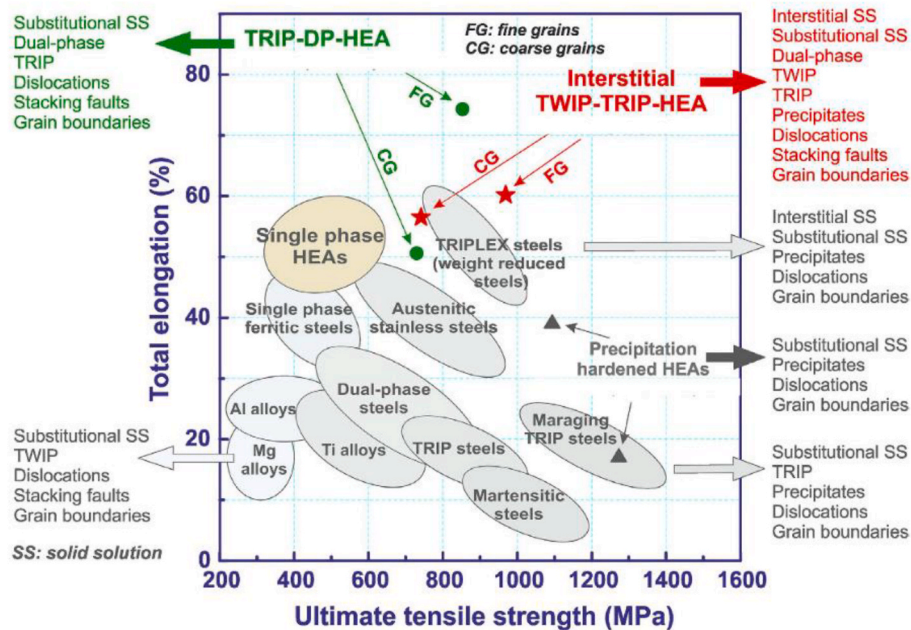


Fig. 15. Relationship between ultimate tensile strength with total elongation of various metallic alloys with various microstructural and deformation mechanisms (Courtesy Springer Nature and adapted from Ref. [292] on under Open Access license).

Table 7

Summary of primary strengthening and toughening mechanisms in CCAs/HEAs, including their functional roles, estimated contributions to mechanical performance, and representative literature representing the quantitative values.

Mechanism	Description and characteristic features	Estimated contribution (%)
Solid Solution	Lattice distortion due to atomic size and modulus mismatch among multi-principal elements	25–35 [232,256–259, 293,432,493]
Grain boundary	Smaller grains act as barriers to dislocation motion according to the Hall-Petch effects	15–30 [134,194,195, 276,293,348,432]
Dislocation/forest	Dislocation–dislocation interactions contribute to work hardening	10–15 [13,114,128, 293,405,432, 494–499]
Precipitation	Strengthening via coherent/incoherent nanoscale precipitates (e.g., B ₂ , L1 ₂)	10–20 [34,51,81,293, 298,432,500]
Interstitial (C, N, O)	Small atoms like O, C, or N distort lattice locally, impeding dislocations	5–15 (up to 25) [151, 169,170,177,274,275, 281,282,293,421,432, 472,501]
Back stress	Strain gradients across microstructural heterogeneities cause kinematic hardening	10–25 [422–424]
Nanostructuring/ ultrafine grains	Reducing grain size below 100 nm increases strength, though may reduce ductility	10–20 [89,115,117, 120,232,281,293,432, 502–504]
TWIP	Twins form dynamically under stress, enhancing ductility and strain hardening	10–20 [9,212,293, 405,407,432,505]
TRIP	FCC phase transforms to HCP/BCC under strain, enhancing strain hardening and delaying failure	10–25 [9,10,212,240, 293,405,432,505]
Delamination	In eutectic structures, crack deflection between lamellae absorbs energy	5–10 [293,432]
Crack tip bridging/ deflection	Heterogeneities deflect cracks and increase fracture resistance	5–10 [82,92,293,432, 436,506]
Phase boundary (dual phase)	Phase interfaces obstruct dislocations and resist crack propagation	10–20 [33,116,203, 418,419,507–514]

Mg-, and Al-alloys in both tensile strength and elongation [292]. This exceptional performance is achieved through a combination of strengthening mechanisms, including interstitial and substitutional solid solution strengthening, twinning, transformation-induced plasticity, nanoparticle strengthening, and grain boundary engineering. Consequently, CCAs can be designed with tailored microstructures to break the inverse relationship between strength and ductility, making them ideal for structural applications.

The ability of CCAs/HEAs to achieve unprecedented combinations of strength and ductility stems from a complex interplay of composition, microstructure, and deformation-driven mechanisms. These mechanisms ranging from synergistic effects of solid solution [119,123,185, 203,453–455], interstitial and precipitation strengthening [228,252, 325,360–367,518] to more advanced effects such as TRIP/TWIP and hetero-deformation-induced (HDI) back stress strengthening do not operate in isolation but often synergize to overcome the classical strength–ductility trade-off. Some of the dominant strengthening and toughening strategies are summarized in Table 7. It provides estimated quantitative contributions to mechanical performance and representative case studies. This comparative overview serves as a mechanistic map and a design toolkit, offering insights into how tailored microstructures and controlled metastability can be used to engineer CCAs with targeted performance envelopes for structural and functional applications. The exact contribution varies with alloy system, processing and test conditions with the mechanisms often being synergetic hence the percentages are not strictly additive.

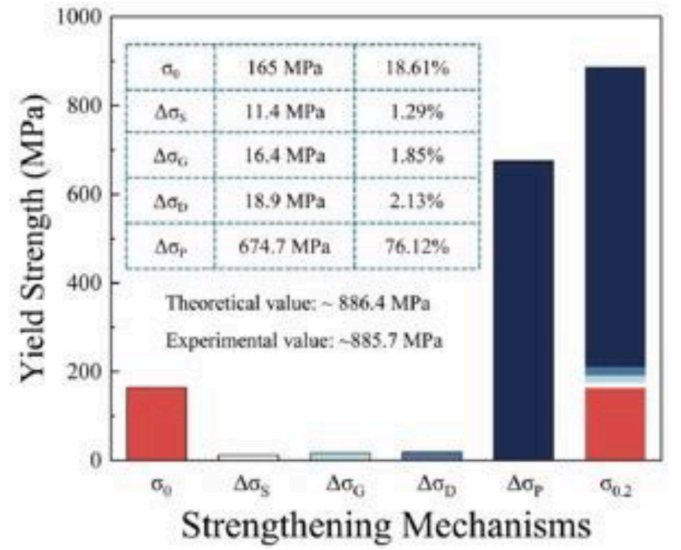


Fig. 16. Cumulative effects of different strengthening mechanisms to CoCr-Fe0.25Ni1.75Nb0.2 CCA/HEA with over 75 % strengthening mechanisms attributed to D022 nanoprecipitates aged for 24 h (Adapted from Ref. [364] with permission No. 6046750262680).

Various alloy systems can be engineered to contribute more than 50 % of the overall strengthening. Typical example is the precipitation strengthening of ~70 % observed in CoCrFe0.25Ni1.75Nb0.2 with the characteristic olive-like D0₂₂ nanoprecipitate [364]. The effects of all the strengthening mechanisms are given in Fig. 16 [364]. Apart from 19 % of the total strength resulting from the intrinsic strength of the matrix microstructure, strengthening from solid solution, grain boundary and dislocation were below 10 %. This is due to aging for 48 h and alloying with Nb increasing the stacking fault energy and drastically reducing the energy barrier for the formation of dislocations with the enhanced strength due to either Orowan strengthening or particle or precipitate shearing resulting from the ordering and coherency strengthening given in Equations (11) and (12). Combined effects of pre-straining and aging heat treatment increase the yield strength and ultimate tensile strength (UTS) of the (CoCrNi)₉₄Ti₃Al₃ alloy [371]. The yield strength (σ_y) is influenced by intrinsic lattice strength (σ_i), solid solution strengthening ($\Delta\sigma_s$), grain boundary strengthening ($\Delta\sigma_G$), and precipitation strengthening ($\Delta\sigma_P$) (Equation (13)). In these MEAs with a consistent matrix structure and composition, $\Delta\sigma_i$ and $\Delta\sigma_s$ are negligible, making grain boundaries and precipitates the primary factors determining mechanical property variations [364].

Achieving superior strength–ductility synergy in non-equiatomic and metastable CCAs requires coupling the various mechanisms. As shown in Table 8, combining these mechanisms significantly enhances yield and tensile strength with minimal loss in ductility. This shows the critical role of synergistic strengthening and toughening strategies in overcoming the strength–ductility trade-off. This is mainly a function of the composition – processing – microstructure pathways. In terms of composition, the non-equiatomic and metastable CCAs are the most suitable and accompanied by hot or cooling working with tailored heat treatment protocols to induce the desired microstructure.

$$\Delta\sigma_{\text{ordering}} = \left(\frac{\gamma_{APB}}{2b}\right) \left\{ \left[\frac{4f\gamma_{APB}}{\pi T} \left(\frac{\sqrt{6}Rh}{3} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} - \beta f \right\} \quad (11)$$

$$\Delta\sigma_{\text{coherency}} = 1.7MG|e|^{\frac{3}{2}} \left[\frac{h^2 f (1 - \beta)}{2bR} \right]^{\frac{1}{2}} \quad (12)$$

$$\Delta\sigma_y = \Delta\sigma_i + \Delta\sigma_s + \Delta\sigma_G + \Delta\sigma_P \quad (13)$$

Table 8

Interplay of composition-processing-structure driving mechanisms contributing to strength – ductility synergy in non-equiatomic CCAs.

Chemical Composition	Processing	Initial Phase	Dominant strengthening mechanisms	Rough Estimate for change in YS/UTS/El (%)	Ref.
Fe50Mn30Cr10Si10	Hot rolling (68 %) + Annealing (1100 °C)	FCC	Substitution of Co with Si solid solution	37/28/103	[515]
Co40Cr25Fe15Ni15Mo5	Hot forging (50 %) + Cold rolling (40 %) + Annealing (1000 °C)	FCC	Strong solid solution induced by Mo with large atomic radii	69/19/20	[516]
Co50Cr25Fe10Ni10Mo5	Hot rolling (50 %) + Cold rolling (40 %) + Annealing (1000 °C)	FCC	Strain-induced martensitic transformation	49/53/203	
Fe46Co30Cr10Mn5V2Si7	Cold rolling (60 %) + Annealing (900 °C)	FCC + HCP (12 vol%)	Substitutional solid solution of V with Si	16/35/-13	[517]
Fe47Co30Cr10Ni5V2Si6	Cold rolling (80 %) + Annealing (900 °C)	FCC	Martensitic phase transformation	-3/54/29	[94]
Co51Cr25Al8Fe8Ni8	Hot rolling (67 %) + Aging (1050 °C)	FCC + NiAl	Precipitation hardening by NiAl	136/-40/-24	[580]
Fe41.3Mn27.3Cr14.3Ni9.3Si4.3Ti3.5	FSA + Aging (900 °C)	FCC + Ni ₃ Ti	The addition of Ti to form Ni ₃ Ti	33/32/9	[16]
Fe37.5Ni30Co22.5Al5Ti5	Aging (800 °C)	FCC + L1 ₂	Precipitation and TRIP	192/117/-29	[518]
Fe42Mn28Co10Cr15Si5	FSP	FCC + HCP	Grain refinement	137/91/71	[519]
Fe46Co30Cr10Mn5V2Si7	Cold rolling (60 %) + Annealing (900 °C)	FCC	Deformation-induced martensitic transformation	148/8/5	[520]
Fe50Mn30Cr10Co10	Cold rolling (60 %) + Annealing (900 °C) + Cold rolling (10 %) + Annealing (750 °C)	FCC	Grain boundary engineering via TRIP	56/25/23	[521]
Fe45Co35V10Cr10	Cold rolling (70 %) + Annealing (750 °C)	FCC	Bimodal structure	113/30/-21	[139]
Fe49.5Mn30Co10Cr10Co0.5	Cold rolling (67 %) + Annealing (400 °C)	FCC	Heterogeneous structure	161/65/-75	[300]
Fe30Cr25Co25Mn10Ni10	Cold rolling (60 %) + Annealing (800 °C)	FCC + Sigma	Different hierarchical structures	185/44/30	
Fe49.5Mn30Co10Cr10Co0.5	Cold rolling (60 %) + Annealing (900 °C)	FCC + M ₂₃ C ₆	Joint TWIP/TRIP with mechanisms	103/32/20	[282]
Fe50Mn30Co10Cr10 (30 ppm B)	Cold rolling (50 %) + Annealing (650 °C)	FCC	Interstitial strengthening with the TWIP and TRIP effects	75/17/-6	[522]

6.3.1. Back stress and the multifaceted mechanisms to strength-ductility synergy

Back stress strengthening is a multifaceted mechanism that significantly contributes to the strength-ductility synergy in CCAs. The combined effects of GND accumulation, microstructural design, and solute interactions create a robust framework for enhancing the mechanical properties of these advanced materials. Back stress strengthening primarily occurs due to the local stress fields generated by atomic size and elastic mismatch among the multiple alloying elements [348,422–424, 523]. These stress fields hinder dislocation movement, increasing resistance to deformation and thus enhancing strength [422–424]. This is by the accumulation of geometrically necessary dislocations (GNDs)

during plastic deformation, leading to the development of internal stresses that counteract further dislocation motion [344–346,524]. As dislocations move through the microstructure, they encounter obstacles such as grain boundaries or precipitates, leading to an increase in GND density [326,327,346,347,528]. This accumulation of GNDs generates back stress, which enhances the resistance of the material to further deformation.

In gradient nano-grained metals, dislocation-interface interactions generate significant back stress, contributing to material strength. In ultrafine-grained MEAs, high back stress during early deformation enhances strain-hardening capabilities [348]. The Hall–Petch equation, related to dislocation pileups at grain boundaries (GBs), produces

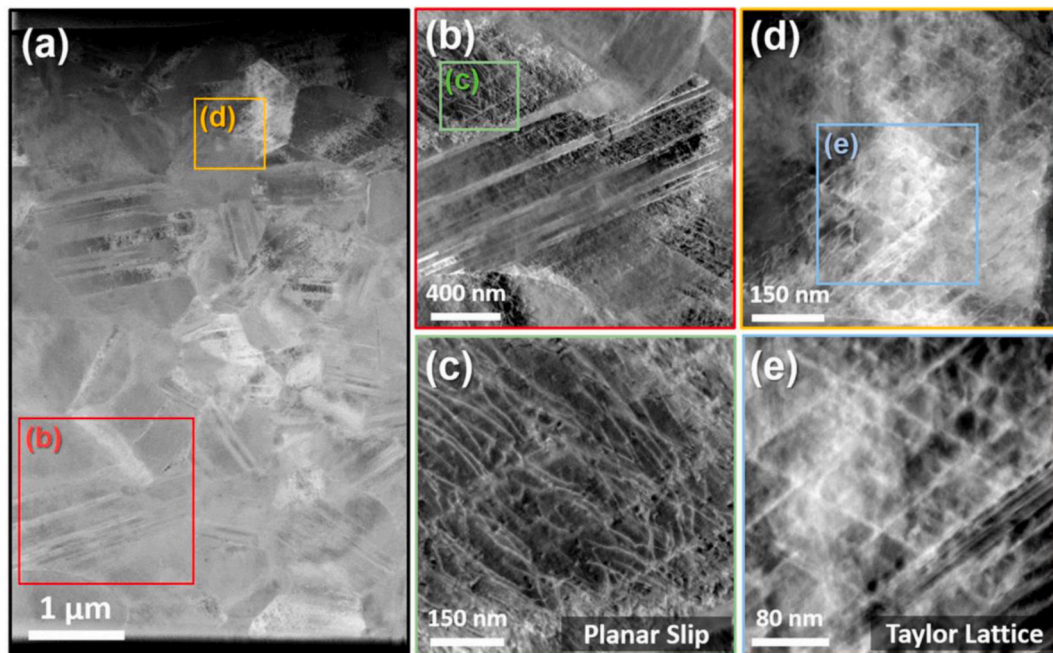


Fig. 17. Microstructural characterization of ultrafine VCoNi showing (a) STEM micrograph of the deformed VCoNi, (b) planar slip of dislocation walls near the grain boundary with a high angle annular dark-field (HAADF) image, (c) magnified region of the area enclosed in the green box, (d) HAADF nano-sized dislocation substructure resulting from non-coplanar slip walls intersecting and (e) magnified region enclosed in the blue box in (d) (Open access [348]).

long-range internal stresses, or back stresses [528]. The high Hall–Petch slope in VCoNi alloy is due to strong GBs that obstruct dislocation movement, causing significant pileups and high back stress during plastic deformation [161,218,348,529,530]. Fig. 17 shows dense dislocation pileups in a planar array from the GB, indicating a major role of back stress in strain hardening [408,409].

In FCC alloys, strain hardening results from isotropic hardening via forest dislocations and kinematic hardening from dislocation accumulation at GBs [528,531,532]. Kinematic hardening depends on the interaction between back stress and forward stress across GBs, with back stress needing to exceed forward stress for synergistic hardening [423]. The back stress contribution is largely determined by the cross-slip probability of the material (P), and back-stress hardening (σ_b) can be modelled as a function of dislocation density (ρ) and strain (ϵ) using Equations (14) and (15) [528,533].

$$\frac{d\sigma_b}{d\epsilon} = \frac{M\alpha Gb}{2\sqrt{\rho}} (1 - P) \frac{d\rho}{d\epsilon} \quad (14)$$

$$\frac{d}{d\epsilon} = M \left(\frac{1}{bd} + \frac{k}{b} \sqrt{\rho} \right) \exp(-\beta\sqrt{\rho}) \quad (15)$$

Where: M = Taylor factor, α = constant in the Taylor equation, G = shear modulus, b = Burger's vector, P = probability of cross slip ($0 \leq P \leq 1$), k and β are model parameters estimated from experiments.

From Equations (14) and (15), a decrease in P enhances the contribution of back stress to strain hardening [528,533]. The solute solutions in CCAs reduce P by increasing the spacing between Shockley partial dislocations, promoting planar slip during deformation. Thus, CCAs benefit from strong back-stress hardening (solute back strengthening) [422–424]. In the UFG VCoNi alloy which was designed for maximized solid-solution strengthening and showed high slip planarity (Fig. 17(b) and (c)) [348], high back-stress hardening contributed significantly to strain hardening in the early deformation stages at lower d values.

The interplay between back stress and microstructural features in CCAs significantly enhances mechanical performance. The optimization of back stress strengthening is achieved through microstructural design, such as heterogeneous structures with fine and coarse grains or layered configurations, which promote dislocation pileups at interfaces [523, 534,548]. High interface density in these materials is crucial for maximizing back stress, leading to improved mechanical properties. For instance, lamellar structures in HEAs demonstrate a unique combination of strength and ductility due to the synergistic effects of back stress and dislocation hardening [348,523]. Back stress also stabilizes the FCC phase and delays deformation twinning, contributing to the strength-ductility balance during deformation.

Specific alloying elements in HEAs can further enhance back stress through solute-dislocation interactions, particularly in multi-principal element alloys [348,523]. Combining back stress strengthening with mechanisms like TRIP amplifies strain hardening, as seen in NbC-reinforced FeMnCoCr HEAs [535,536], where even low dislocation density structures exhibit high strain-hardening rates. This synergy allows alloys to endure greater deformation without failure, providing both strength and ductility, making them suitable for demanding applications.

Some promising families of CCAs and their mechanisms contributing to strength-ductility synergy are listed in Table 9. CCAs with dominant FCC structures generally exhibit lower strength compared to their BCC counterparts. However, through compositional adjustments and thermomechanical postprocessing, a significant balance between strength and ductility can be achieved. The key factor in this synergy is the presence of chemical and microstructural heterogeneities, which disrupt traditional deformation mechanisms [526,527]. Additionally, the accumulation of geometrically necessary dislocations and the Zener pinning effect from the B2 and other precipitates are commonly observed in many of these alloys [526,527]. As a result, CCAs offer an

Table 9

Typical CCAs/HEAs with strength-ductility synergy and underlying mechanisms.

Composition	Strength (MPa)	Ductility (%)	Mechanisms
CoCrFeNi	267–650	96.2	Solid solution strengthening, multiple slip interactions with TRIP
CrMnFeCoNi	300–800	73	Low stacking fault with planar slip and twinning
Dual-phase HEA	1500–1900	18.4	Hetero deformation induced strain hardening and phase boundary buffering
AlCoCrFeNi _{2.1}	944	25.6	Eutectic microstructure and solid solution strengthening
CoCrFeMnNi	800 – 1300	15 – 30	Nanotwinning, dislocation slip, intrinsic and extrinsic toughening [442]
TiZrHfTaNb	1200 – 1600	2 – 5	Predominantly BCC with limited ductility due to casting [537]
CoCrFeMnNi	800 – 1200	12 – 25	Heterogenous microstructure and TWIP [538,539]
CrFeNiCo	600 – 900	20 – 40	Solid solution and dislocation strengthening
CrCoNi	700 – 1100	10 – 20	Dynamic strain aging and dislocation mechanisms
AlFeCoNi	600 – 950	8 – 15	Eutectic microstructure and phase-specific work function
FeCoNi	500 – 850	15 – 35	Grain boundary strengthening and precipitation hardening
(FeCoNi)Al ₆ Ti ₇	800 – 1300	20 – 25	Grain refinement and dislocation pinning by L ₁₂ nanoparticles [540,589]
(FeCoNi)Al ₇ Ti ₇	1200 – 1500	40 – 50	Ultrafine grain with 50–55 % volume fraction of L ₁₂ nanoparticles [541]
NiCoFeCrAlTi	1700	>51	Nano-spaced stacking faults and three stage strain hardening [187]
TiZrHfNiCu	1000 – 1400	5 – 10	BCC with low ductility
CrCoNi	800 – 1000	25 – 35	Grain refinement (~2μm) low initial dislocation density, dense grain/twin boundaries and multiple slip systems [543]
CrCoNi	1200 – 1500	20 – 25	HDI hardening with gradient nano-grained (GNG) structure ranging from ~50 nm to ~1.3μm with low SFE [543]
VCoNi	955 – 1700	26 – 50	Heterogenous structure of fine and ultrafine grains producing high back stress strengthening, Hall Petch effects and low cross slip [348]
N-doped VCoNi	1100 – 1500	26	Grain refinement strengthening from the nitrogen alloying and strengthening from annealing twins, deformation twins and multiple twinning systems [27]
FeCrAlNi	1150 – 3300	>40	HL with high-density nanosized precipitates [544]
CoCrFeMnNi	900 – 1300	15 – 30	Multiple dislocation slips and deformation twinning
AlCoCrFeNi _{2.1}	800 – 1200	10 – 30	Heterostructure of BCC (B2) and FCC (L ₁₂) lamellae [545, 546]
(FeCoNiCr) ₉₄ Ti ₂ Al ₄	850 – 1000	30 – 45	Nanosized FCC(L ₁₂) coherent precipitates after annealing [547]
AlCrCuFeMnNi	800 – 950	25 – 40	Nanosized L ₁₂ coherent precipitates [547]
CrFeCoNiAlTi	1650 – 1750	18 – 23	Precipitation and heterogeneous induced strengthening [140].
(TiZrHf) ₈₇ Ta ₁₃	1300	24	Martensitic twinning with $\beta \rightarrow \alpha$ transformation, high work

(continued on next page)

Table 9 (continued)

Composition	Strength (MPa)	Ductility (%)	Mechanisms
N-doped TiZrNbTa	1300 – 1400	18 – 20	hardening rates and self-accommodation [548] Interstitial strengthening, in-situ grain refinement, planar dislocation cross slip and nanosized precipitates [549]
FeNiCoAlTaB	590 – 1050 330 – 1400	23 – 25 35 – 43	HL structure [550,551]
CoCrFeNiNb	1000 – 1600	12 – 28	HL with ductile FCC and Laves [552]
FeNiCoAl	1200 – 1400	20–30	HL with solid solutions, interface, precipitates and martensitic transformation [102]
FeNiCoAlTaB	890 – 1100	23 – 45	HL with fine and ultrafine grains with B ₂ (NiAl) precipitates resulting in Zener pinning effect [248,550]
FeNiCoAlCrB	700 – 900	22 – 38	HL with ultrafine FCC and fine B ₂ promoting Zener pinning effect [429]
AlCoCrFeNi	1400 – 1600	14 – 20	

[HL – Heterogeneous lamellae].

innovative solution to the strength-ductility trade-off in metallic materials and hold the potential to continuously drive advancements in structural and functional material design.

6.3.2. Twinning and transformation induced plasticity mechanisms

The interplay between dislocation dynamics and phase transformations plays a crucial role in the mechanical behavior of HEAs.

These mechanisms have been explored to induce strength – ductility synergy [93,100,108,115,377,415,416]. The concept of twinning and transformation induced plasticity mechanisms (TWIP/TRIP) were used to improve structural and functional properties of austenitic stainless, low density and TWIP steels [46,47,554555]. The TWIP/TRIP mechanisms take advantage of extra plasticity effects by modifying the stacking fault energy (SFE) of the system [52,54,106,174,377,490,556–561]. In CCAs/HEAs, emphasis is on tailoring the metastability of the phases instead of stabilizing the phases or ensuring the formation of single phases. Being plasticity mechanisms, TWIP/TRIP are dependent on sizes, morphology and distribution of the grains [16,108,300,415]. Hence, the mechanisms can be induced simultaneously by engineering the alloy compositions, grain size and deformation conditions which correlates with SFE [21,52,74,106,377,556–561].

The schematics showing the deformation mechanisms of CCAs driven by combined TWIP and TRIP mechanisms is given in Fig. 18 [563]. Starting with an FCC matrix strengthened by solid solution effects and precipitates, increased local strain, especially at lower temperatures, activates stacking faults leading to deformation twins (TWIP). Further straining induces HCP martensite nucleation and growth (TRIP) due to stacking fault interactions and phase instability [52,54,106,174,377,556–561]. These concurrent mechanisms enhance strain hardening, delaying plastic instability and improving strength–ductility. The schematic also plots stacking fault energy (SFE) versus temperature, contextualizing the dominance of TWIP or TRIP across various alloy systems.

The effects of stacking faults in contributing to TWIP/TRIP as a function of alloying elements is pronounced in CCAs and conventional alloys. Stacking faults are crystallographic defects characterized by disruptions in the regular sequence of atomic planes within a crystal

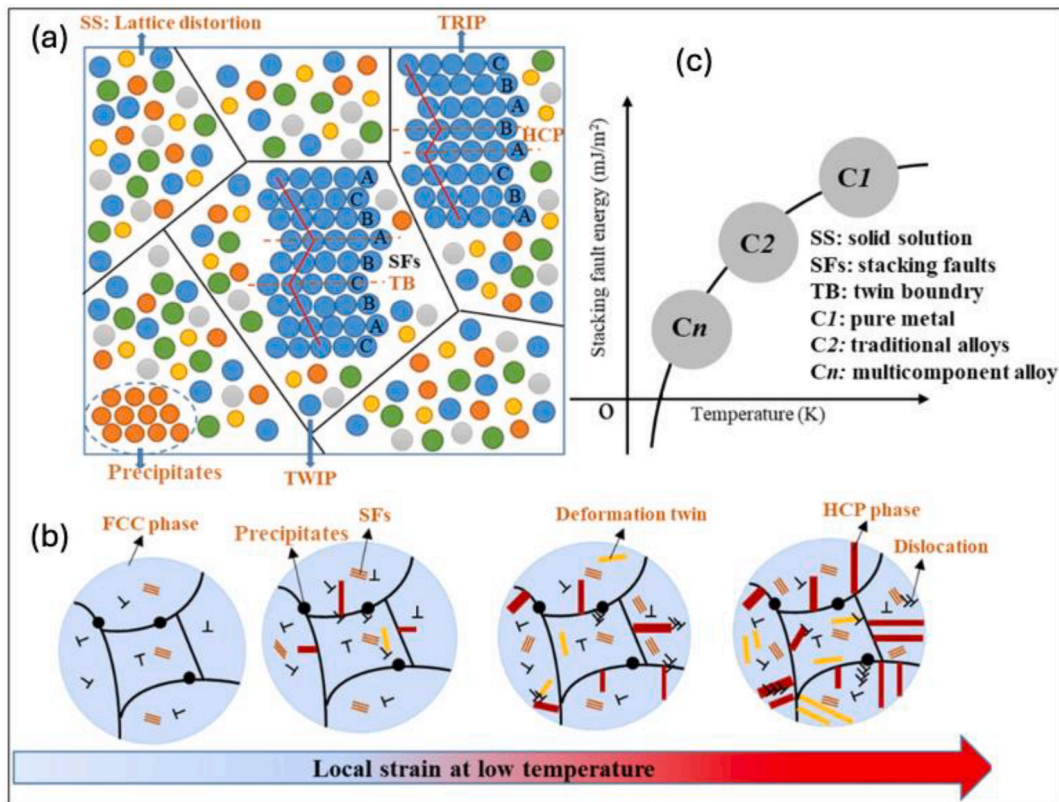


Fig. 18. Schematic illustration of the TWIP and TRIP mechanisms operating in FCC-based CCAs with: (a) atomic-scale features including solid solution inducing lattice distortion (SS), stacking faults (SFs), twin boundaries (TBs), and HCP phase formation under increasing strain (b) sequence illustrates the evolution of microstructure from an FCC matrix through SF and deformation twinning to strain-induced phase transformation (TRIP) and (c) the relationship between SFE and temperature across alloy types showing the influence of SFE on the activation of TWIP and TRIP mechanisms (Courtesy Springer and adapted from Ref. [563] with permission No. 6046751083673).

Table 10
Typical SFE ranges and their effects on deformation mechanisms [564–567].

SFE ranges (mJm ⁻²)	Characteristic of deformation mechanisms
>40	Favours dislocation slip
20 – 40	Favours TWIP effects by reducing the critical resolved shear stresses
<20	Favours the transformation from FCC to HCP (TRIP effects)

structure. In ideal crystals, atoms follow a specific, repeating pattern, such as the ABCABC sequence in face-centered cubic (FCC) structures. A stacking fault occurs when this sequence is interrupted, altering the local atomic order [562]. These defects significantly influence material properties, including strength and ductility. In FCC crystals, a full dislocation on the (111) plane can split into two partial dislocations, creating a stacking fault region with associated stacking fault energy (SFE). A larger separation between partial dislocations reduces SFE, affecting deformation mechanisms. High-SFE materials favour dislocation recombination and cross-slip, leading to wavy-slip configurations, while low-SFE materials promote planar slip and deformation twins (DTs) [52,54,100,106,174,377,556–561,563]. This distinction impacts work hardening behavior, with high-SFE metals exhibiting decreasing hardening rates and low-SFE metals enhancing strength-ductility synergy.

The SFE strongly affects mechanical behavior by governing dislocation glide, cross-slip, and twin formation. When SFE is high (>40 mJ/m²), the mechanisms that dominates is the dislocation glide, whereas low SFE (<40 mJ/m²) favours twinning and can further enhance the TRIP effect (Table 10) [564–567]. The SFE for most equiatomic CCAs/HEAs are in the range of 18–30 mJ/m² – the domain favourable for twinning deformation mechanisms [97,99,434]. For the non-equiatomic alloy systems based on Co – Cr – Fe – Mn – Ni compositions, the SFE ranged from 57.8 to 101.6 mJ/m² [434]. However, the deformation mechanisms of CCAs/HEAs cannot be mainly predicated on the intrinsic SFE as observed in the TRIP Co₁₀Cr₁₀Fe₄₀Mn₄₀ alloy which was wrongly identified as TWIP [568]. Local chemical ordering (LCO) in CCAs/HEAs significantly influences the SFE, with increasing LCO leading to a wider range of SFE values and their corresponding effects on deformation mechanisms (Table 10) [564–567]. The LCO also

contributes to the critical stress required for dislocation slip and affects dislocation storage in bulk materials. In CCAs, dislocations must continuously overcome the activation barriers imposed by LCO, which enhances strain hardening and promotes a strength-ductility synergy in single-phase MEAs/CCAs [37,276,294,479,480,569].

Stacking faults have been engineered in CrCoFeMnNi alloys for strengths as high as 1 GPa with 60–70 % ductility ranges [9,12,195]. During early deformation, Shockley partial dislocations (1/6<112> type) were active near the crack tip, leading to the formation and movement of stacking faults (SFs) [9,12,443,494]. Fig. 19 shows the in-situ processes, with SFs on {111} planes continuously forming and dissolving, indicating easy partial dislocation movement [442]. Fast Fourier transforms confirmed the [110] zone axis, allowing direct imaging of fcc stacking (Fig. 19 (e)) [442]. Partial dislocations on {111} planes left SFs that transitioned to a hexagonal close-packed structure, later removed by trailing dislocations [442]. These findings demonstrate that, due to low stacking fault energy, partial dislocation slip, and SF formation are crucial for strain accommodation during early plastic deformation [9,12,443,494], while their interactions create obstacles that contribute to hardening (Fig. 20) [442].

The SF parallelepiped observed from tilting angles of 0 and 25 showed the role of the partial dislocations (Fig. 20) [442]. Two partial dislocation systems are activated on parallel planes, forming a dislocation rhomboid – a volume defect that causes dislocation tangling. While partial dislocation movement initially allows easy deformability, their interactions lead to significant strain hardening by creating stable three-dimensional stacking-fault defects that pose substantial obstacles to other dislocations.

Microstructural tailoring in CCAs/HEAs with low SFE (<40 mJ/m²) enables TWIP/TRIP or dual/triple-phase microstructures. This enhances strength-ductility synergy. In FCC HEAs/MEAs, reduced SFE promotes deformation twinning (DT), multiple slip systems [486], and improved work hardening, as observed in CrCoNi [116,117,134] and B-doped FeMnCoCr alloys [522]. These effects underpin the TWIP mechanism, while TRIP effects in Fe-Mn-Co-Cr [570] and FeCoCrNiVSi HEAs [100], driven by phase transformations and grain refinement [67,100,570], ensure continuous work hardening, crucial for strength-ductility synergy. Additionally, TRIP CCAs enhance phase stability and optimize deformation mechanisms based on the dominant phase in the

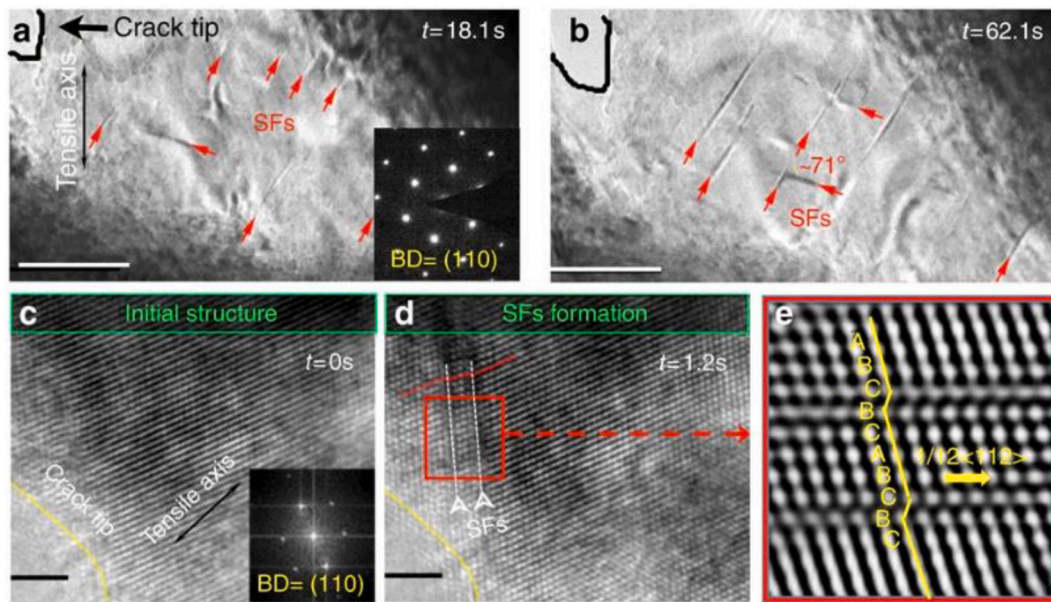


Fig. 19. Stacking fault and partial dislocations of CrCoFeMnNi with (a) and (b) TEM images of the formed stacking faults in the beam direction of [110], (c) and (d) in-situ high resolution showing multiple SFs at the atomic scale at the crack tip and (e) atomic structure and stacking sequence of SF from inverse fast Fourier transform image (Courtesy of Nature and adapted from Ref. [442] under Open access license).

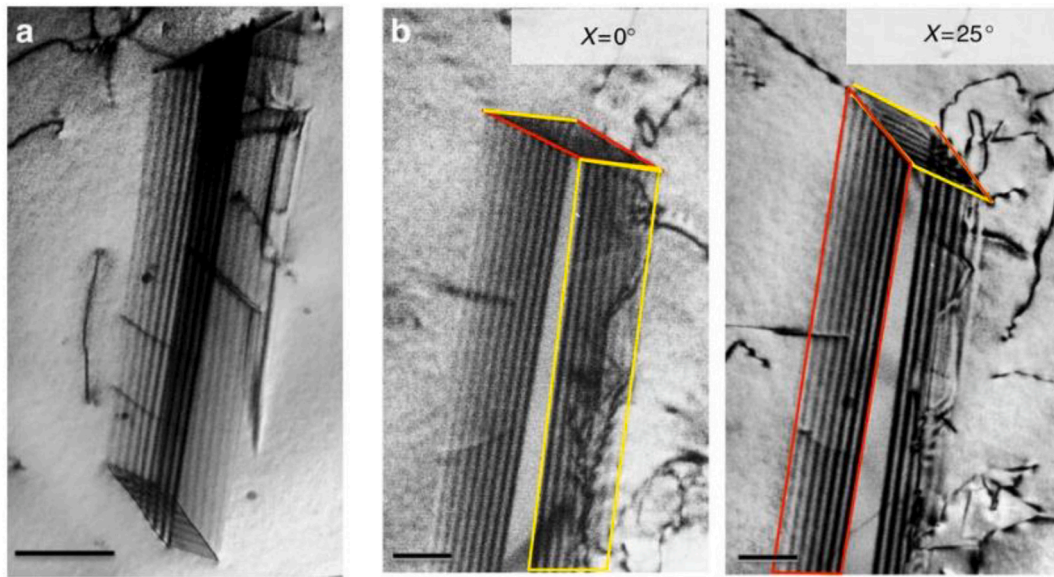


Fig. 20. Typical stacking fault parallelepipeds showing (a) 200 nm scale TEM of SF on three sets of {111} planes and (b) at x-tilting angles at 0° and 25° (Courtesy Nature and adapted from Ref. [442] – Open access).

Table 11

The mechanisms of TWIP and TRIP with synergistic effects on strength and ductility of CCAs/HEAs systems.

Mechanism	Contribution to strength	Contribution to ductility
TWIP	Increased work hardening by twinning [522,563]	Improved ductility through deformation twins [433,563]
TRIP	Continuous work hardening through phase transformation [67,570]	Enhanced ductility via phase transformation at grain boundaries [100,415]
Combined	Synergistic TWIP/TRIP activated [16,137,433]	High ductility is achieved through dynamic Hall – Petch effect resulting from the planar slip activities and twinning

microstructure to achieve exceptional strength and ductility [292,490]. Typical effects of TWIP, TRIP and the synergistic effects on overcoming strength-ductility trade-offs in next generation structural materials is given in Table 11. The key differences between TRIP and TWIP mechanisms in CCAs/HEAs are their distinct deformation processes and resulting mechanical properties. These alloys enhance strength-ductility synergy through tuneable performance and microstructural tailoring. A combined effects of TWIP and TRIP can achieve ductility up to 50 % with tensile strength exceeding 1 GPa [123,481]. However, ongoing research should focus on overcoming challenges in understanding factors that could contribute to reverse Hall Petch effects mechanisms which could lead to strength-ductility trade-off.

The TWIP effect depends on grain size and deformation temperature. In CrCoFeMnNi, a critical grain size of roughly 2–3 μm (Fig. 21(a)) is needed to trigger twinning, while cooling from room to cryogenic temperatures significantly boosts TWIP (Fig. 21(b)) and fosters a strength–ductility synergy in both CoCrFeNi and Co35Cr25Fe20Ni20 (Fig. 21(c)). Moreover, shifting from equiatomic to non-equiatomic composition lowers the stacking fault energy, which enhances twinning, work hardening, and overall mechanical performance (Fig. 21(d)). Thus, the alloy with a stronger TWIP effect has the corresponding higher work-hardening rate, underscoring the importance of mechanical twinning in maintaining plasticity under strain.

Recent advancements in achieving strength-ductility synergy in CCAs/HEAs focus on innovative thermo-mechanical processing (TMP) techniques. This is to allow precise microstructural tailoring (synergistic effects of TWIP and TRIP) for optimal strength-ductility combinations in

both single-phase and multiphase alloys [16,45,94,137,211,417–420,521,522]. Severe plastic deformation processes have also shown significant potential in enhancing this synergy [46,97,153,192,532,533]. Additionally, the overall processing strategy, including rolling and subsequent annealing, plays a crucial role in microstructure and texture evolution [519–521]. Emerging approaches aim to streamline these processes, making it easier and more efficient to achieve the desired balance of strength and ductility in HEAs.

6.3.3. Deformation-induced martensitic transformation mechanism

Ductility primarily depends on enabling dislocation slip and multiplication, which requires effective strain hardening. Strengthening can also be achieved through martensitic transformation, as seen in steels and Ti alloys. Deformation-induced martensitic transformation (DIMIT or TRIP) enhances both strength and ductility by transforming metastable retained austenite (FCC γ phase) into either HCP(ϵ) or BCC (α') martensite during deformation, as schematically shown in Fig. 22 [178]. The TRIP effect, through its strengthening mechanisms provides pathway for deformation-induced martensitic transformation (DIMIT) enhances ductility by increasing resistance to dislocation slip and introducing new interfaces [178]. This boosts strain hardening through dislocation hardening of both the matrix and the martensitic phase [102,203,568].

Slip-assisted phase transformation in CCAs promote stacking faults contributing to strength-ductility synergy. The face centered cubic (FCC) $\rightarrow$ hexagonal closed packed (HCP) and body centered cubic (BCC) $\rightarrow$ FCC transformations within heterostructure nanograins of CCAs are facilitated by the coordinated motion of Shockley partial dislocations [571,572,574,576]. This is schematically shown in Fig. 23 [500,571]. The FCC $\rightarrow$ HCP transition is shown in Fig. 23(a) where there is gliding of multiple Shockley partial dislocations of $1/6 \langle 112 \rangle_{\text{FCC}}$ on alternate $\{111\}_{\text{FCC}}$ slip planes, causing local stacking faults that alter the atomic stacking sequence from the typical ABCABC stacking of the FCC structure to the ABAB stacking characteristic of the HCP structure (hcp showed in Fig. 24(a–e)). This is shown in Fig. 24 for gradient nanostructured Fe₄₅Mn₃₅Cr₁₀Co₁₀ CCA with atomic level fcc $\rightarrow$ hcp $\rightarrow$ bcc phase transformation [502]. The atomic rearrangement through this slip-induced partial dislocation motion effectively converts regions of the FCC lattice into stable HCP phases with three Burgers vectors (Fig. 24(e)). This mechanism highlights how localized slip events at the atomic scale directly induce significant structural transformations

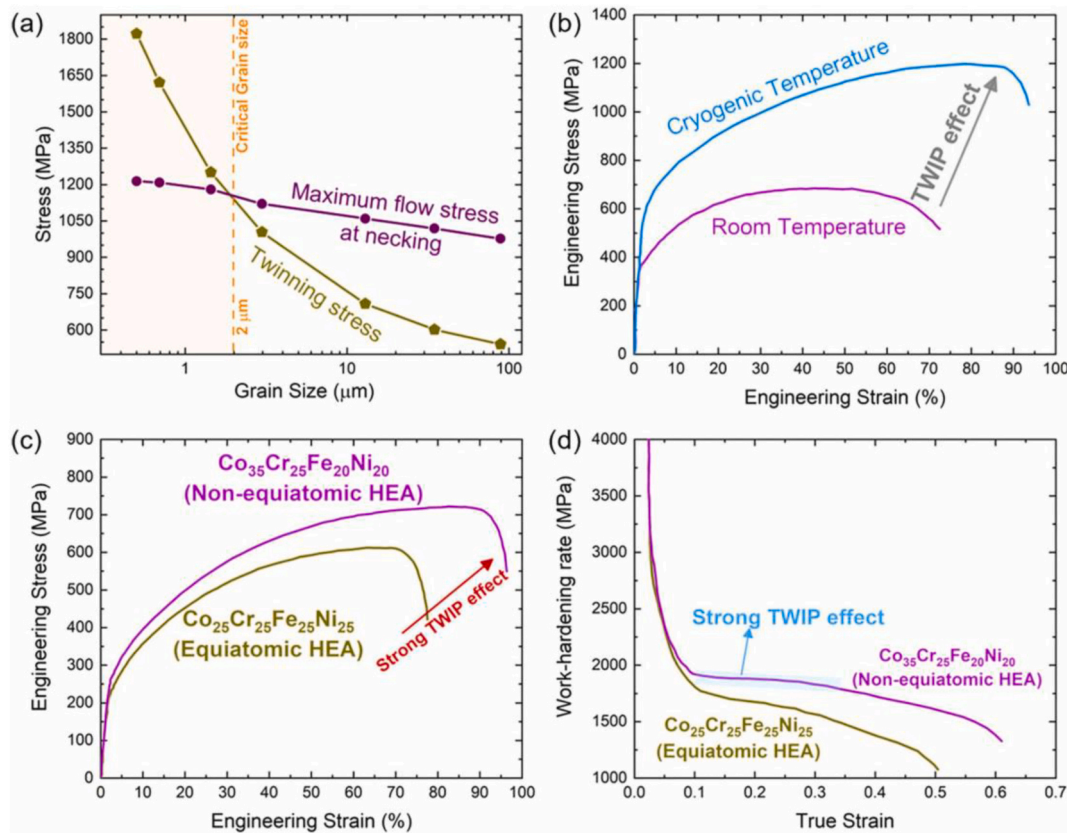


Fig. 21. Characteristics contribution to strength – ductility synergy showing (a) variation of twinning stress and maximum flow stress with grain size, (b) comparison of tensile stress–strain responses at cryogenic and room temperatures, (c) stress–strain behavior for equiatomic and non-equiatomic CoCrFeNi alloys, and (d) correlation of work-hardening rate with true strain with the strengthening contribution of mechanical twinning (Courtesy of Elsevier and adapted from Ref. [95] with permission No. 6046760473062).

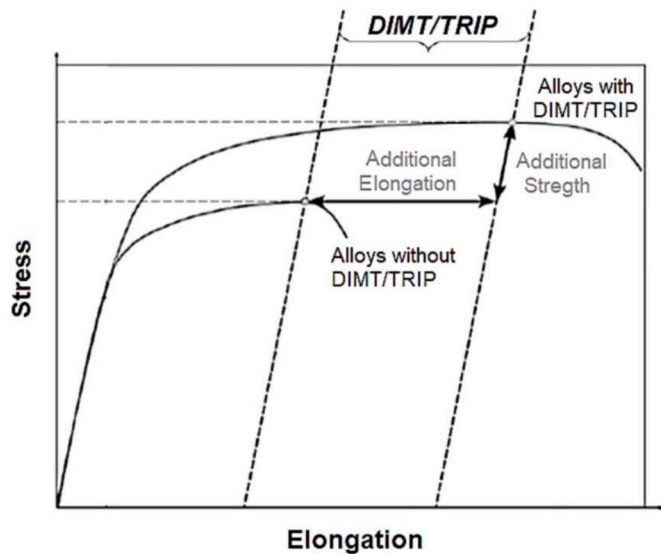


Fig. 22. Effects of deformation-induced martensitic transformation on the strength – ductility synergy in alloys (Courtesy Elsevier and adapted from Ref. [178] with permission No. 6046761067424).

[571–573,575–577], which contribute to enhanced mechanical properties – specifically, increased strength through microstructural refinement and improved ductility by enabling additional deformation pathways.

The slip-assisted BCC → FCC transformation is given in Fig. 23(b).

Dislocation slip occurs along characteristic slip directions such as $\langle 111 \rangle$ in BCC and $\langle 112 \rangle$ in FCC on respective crystallographic planes. The atomic arrangements and interactions with dislocations show how localized slips can initiate phase transitions at the atomic scale. This effectively promote strength-ductility synergy in CCAs by strain accommodation and stress redistribution [572,574], delaying localized failure.

The HCP to BCC transformation, characterized by a shift in atomic plane angles and spacing, notably from $\sim 70.5^\circ$ (HCP) to 90° (BCC), with atomic spacing reducing from 2.33 Å to 2.17 Å is given in Fig. 24(f–k). This phase shift occurs through localized atomic shuffling facilitated by partial dislocation dipoles in perpendicular directions for the formation of semi-coherent phase boundaries between FCC and BCC phases. The fcc → hcp → bcc phase transformation followed Nishiyama-Wassermann (NW) orientation relationship (Fig. 24(l)), generally observed in CCAs and TRIP steels. The NW orientation promotes controlled stress-induced phase transition in the $\text{Fe}_{45}\text{Mn}_{35}\text{Cr}_{10}\text{Co}_{10}$ gradient CCA [571–573].

The FCC → BCC and FCC → HCP transformations that trigger TWIP/TRIP effects are composition- and temperature-dependent. This is evident in the modified Cantor alloy, where shifting from equiatomic $\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{20}\text{Mn}_{20}\text{Ni}_{20}$ to non-equiatomic $\text{Co}_{50}\text{Cr}_{20}\text{Ni}_{20}\text{Fe}_{5}\text{Mn}_5$ improved both strength and ductility (Fig. 25) [101], due to TWIP/TRIP effects arising from a dual-phase (FCC/HCP) microstructure [101] and strain-induced martensitic transformation in metastable CCAs/HEAs [130,178]. The mechanisms driving strength – ductility synergy are more pronounced in non-equiatomic CCAs/HEAs, influencing the work-hardening rate and true strain, as shown in Fig. 26 for the metastable and non-equiatomic $\text{Fe}_{15}\text{Ni}_{8}\text{Mn}_{8}\text{Co}_{3}\text{Ti}$ CCA [130,178]. Thus, tailoring composition and heat treatment induce the microstructural features allowing for dislocation-precipitate interactions, TWIP, and

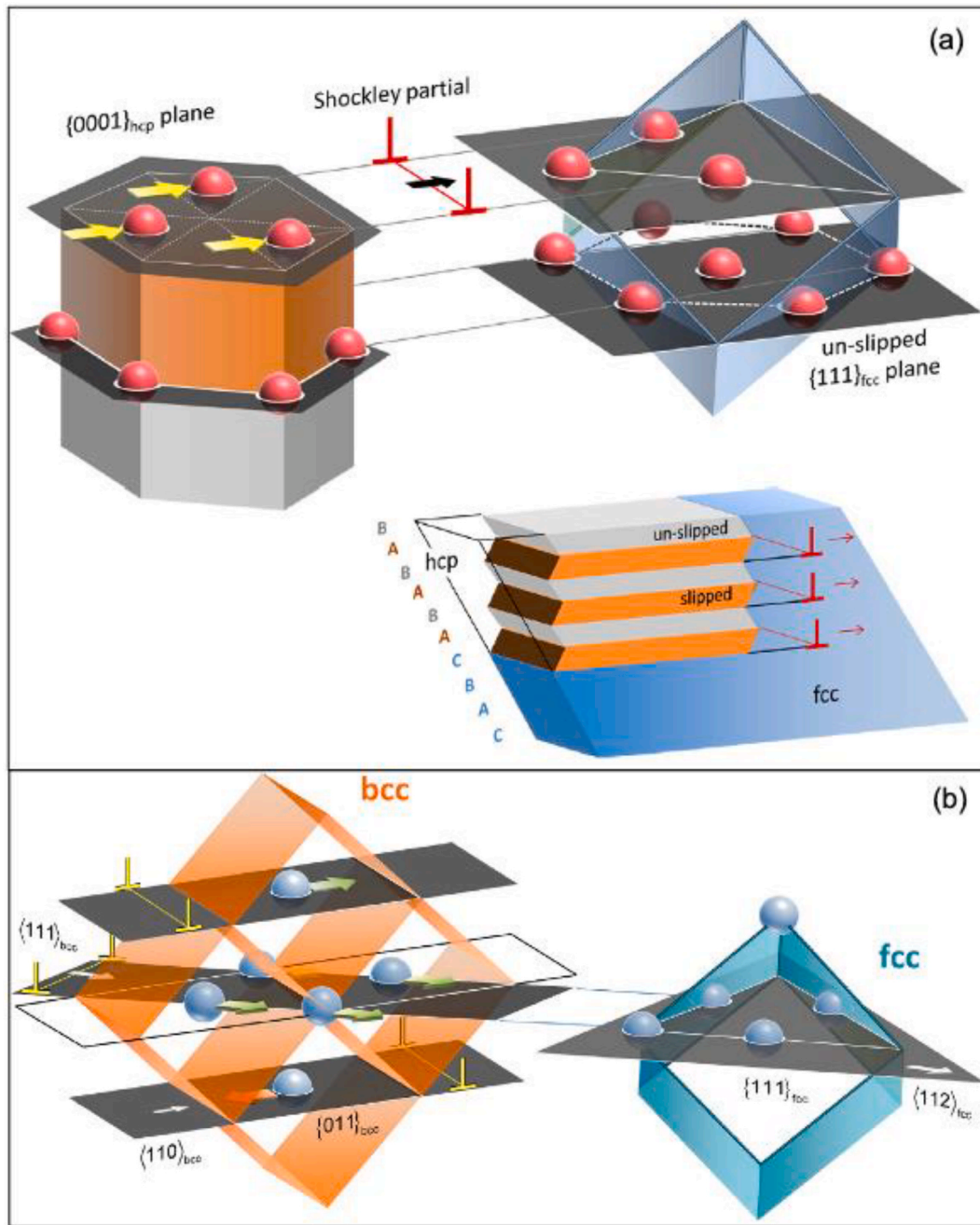


Fig. 23. Schematics of slip-assisted phase transformation showing (a) FCC $\rightarrow$ HCP transition assisted by dislocation gliding and (b) BCC $\rightarrow$ FCC which is assisted by dislocation gliding on parallel planes (Courtesy Elsevier and adapted from Ref. [500] with permission No. 6046770334863).

TRIP collectively shaping the complex deformation mechanism with associated work-hardening behavior of Fe-based CCAs [94,111,129,130,178]. This provides strategic pathway for the design of advanced structural alloys.

Table 12 summarizes key compositional variants of Fe- and Co-based CCAs/HEAs that undergo deformation-induced FCC $\rightarrow$ HCP martensitic transformation enabling superior strength–ductility synergy [178]. Emphasis is on the tailored compositional and microstructural modifications, including non-equiatomic designs and grain size control that activate TRIP and TWIP effects [94,137,211,417–421]. In the Fe-based CCAs, the coexistence of FCC and HCP phases and the presence of TWIP/TRIP mechanisms in Fe50Mn30Co10Cr10 led to UTS above 870 MPa with elongation as high as 75 % [243]. Similarly, Co-based non-equiatomic Co50(FeNi)20Cr25Mo5 achieved UTS above 1130 MPa with

acceptable ductility (percentage elongations above 60 %), primarily due to TRIP-dominated mechanisms within the FCC matrix [441,512,582,583]. Generally, other transition metal-based CCAs had FCC $\rightarrow$ HCP transformation leading to impressive mechanical combinations, such as Fe45Co30Cr10Ni5V5Si3 with 1025 MPa UTS and 84 % elongation. The compositional tuning and deformation mechanisms are critical in overcoming the traditional strength–ductility trade-off in advanced structural materials.

Alloying plays a critical role in tuning the mechanical performance of TRIP-assisted HEAs. Substituting Co or Ni with elements such as Mo, Cr, or CP (carbon-containing phases) in Co- and Ni-based systems (Fig. 27 (a) [509,510] and (b) [580]) modifies phase stability and deformation mechanisms, often enhancing strength and ductility. Similarly, the addition of Si (Fig. 27 (c)) effectively alters stacking fault energy (SFE)

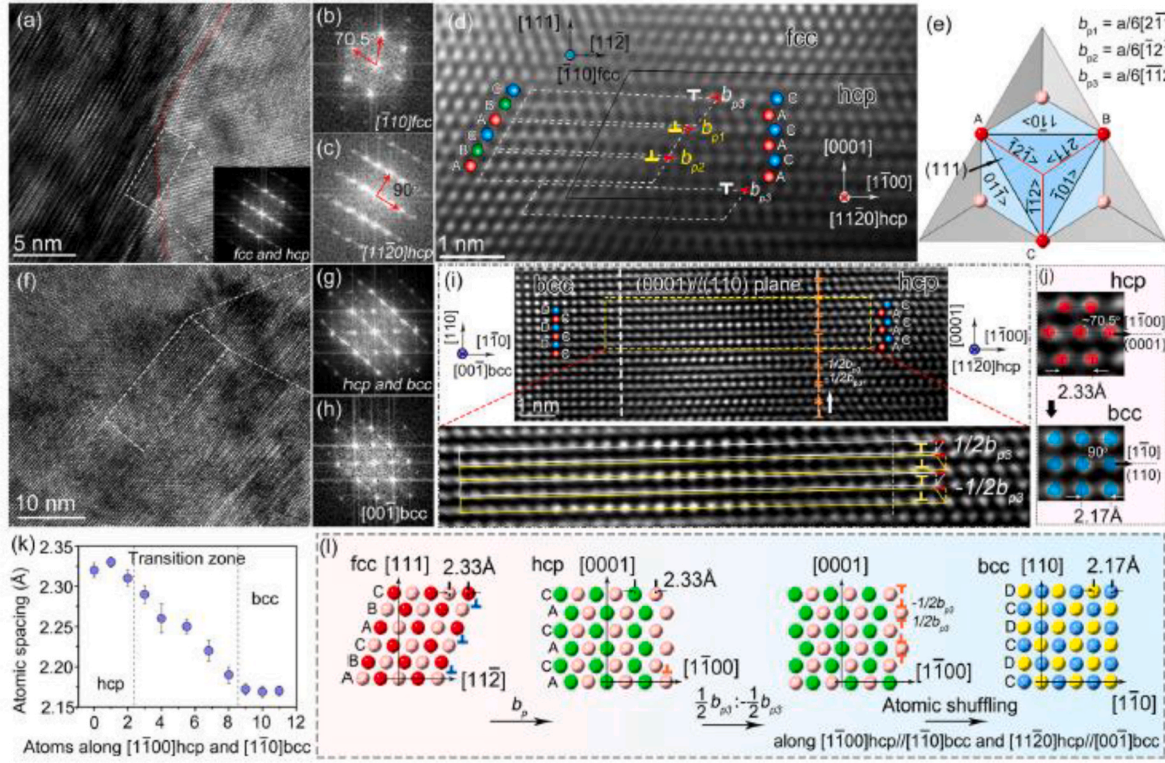


Fig. 24. Atomic-scale analysis of the FCC → HCP → BCC transformation in a gradient nanostructured Fe45Mn35Cr10Co10 showing: (a–b) HRTEM images of the FCC/HCP interface. (c) FFT patterns showing coexisting FCC/HCP, (d) image with Fourier filtering with Shockley partial dislocations driving FCC → HCP transition, (e) Burgers vectors, (f–g) HRTEM and FFT of the HCP/BCC interface, (h) structural shifts during HCP → BCC transition, (i) atomic plane tracking showing angular change from ~70.5° (HCP) to 90° (BCC), (j) Interatomic spacing reduction from 2.33 Å (HCP) to 2.17 Å (BCC), (k) atomic mapping of shifts across the transition zone and (l) schematic of the fcc → hcp → bcc transition mechanisms (Courtesy of Taylor and Francis and adapted from Ref. [573] with permission No. 6046770918124).

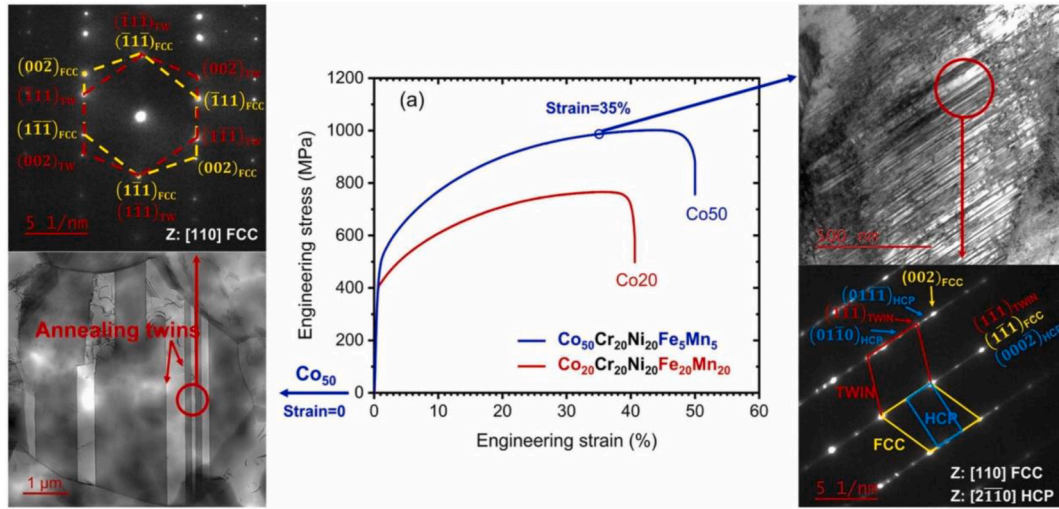


Fig. 25. Microstructural and mechanical comparison between equiatomic Co20Cr20Ni20Fe20Mn20 and non-equiatomic Co50Cr20Ni20Fe5Mn5 alloys showing enhanced strength and ductility in engineering stress–strain curve of non-equiatomic Co50 variant. The TEM and SAED analyses reveal annealing twins, TWIP, and strain-induced FCC → HCP transformation contributing to the superior mechanical performance of the non-equiatomic alloy (Courtesy of Elsevier and adapted from Ref. [101] with permission No. 6046780237084).

[581], enabling controlled γ -to- ϵ martensitic transformation and promoting TRIP effects. In Fig. 27 (d), composition variation in Fe-based CCAs significantly influenced mechanical response, with optimized alloys like Fe60 and Fe62.5 showing high strength and ductility due to enhanced TRIP activity, especially at cryogenic temperatures [582,583].

Minor alloying additions can enhance DIMT for improved strength–ductility synergy. Adding Ti to TWIP

Fe42.8Mn28.3Cr14.8Ni9.6Si4.5 (via friction stir alloying) led to Ni₃Ti precipitation, depleting Ni matrix structure, destabilizing the FCC phase, and lowering SFE. This triggered TRIP after annealing at 900 °C, resulting in a microstructure with enhanced strength and ductility (Fig. 28) [16].

The engineering and true stress–strain curves of Fe47Co30Cr10-Ni5V5Si3 (3Si), Fe47Co30Cr10Ni5V2Si6 (6Si), and AISI 304L is given in

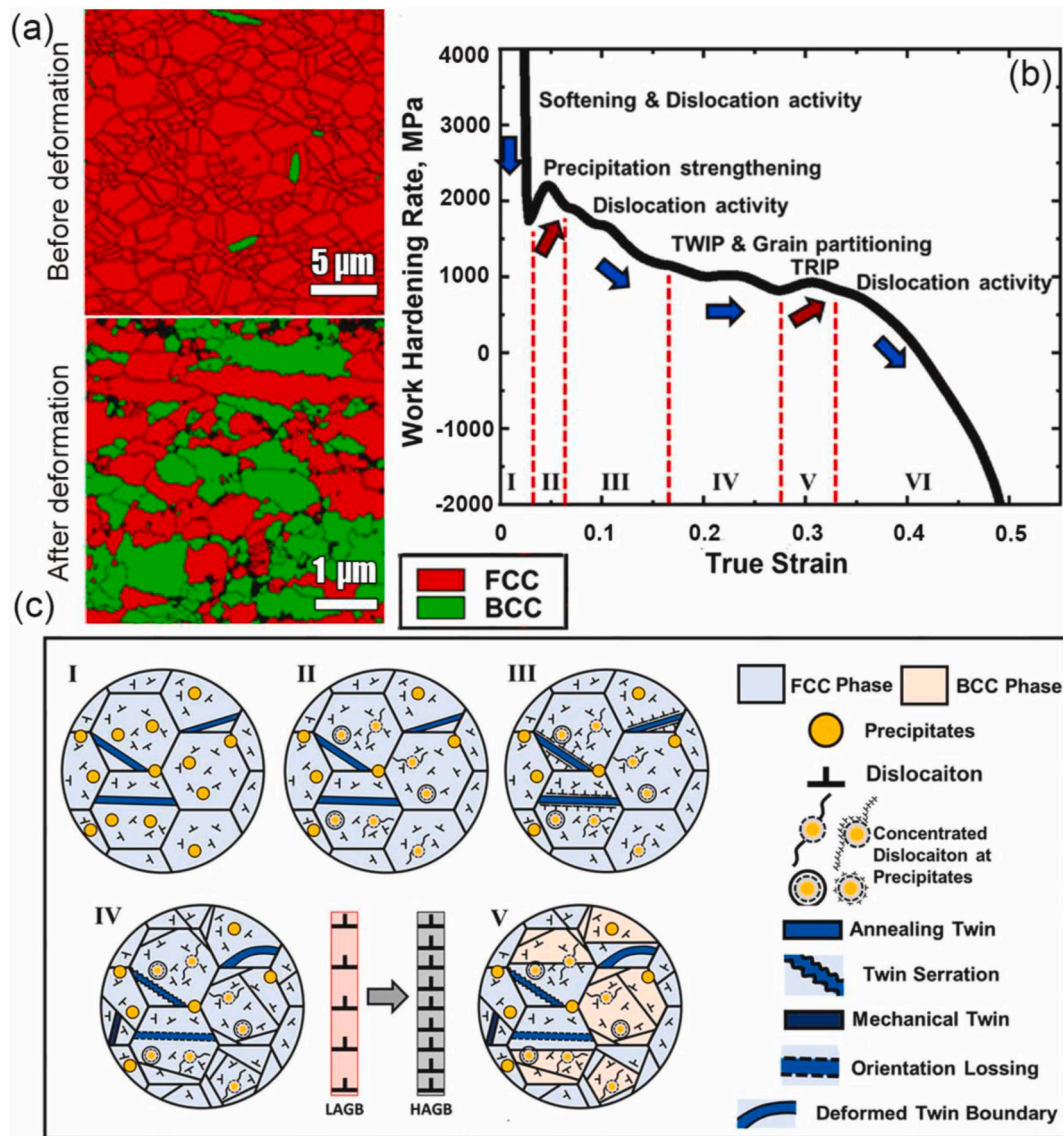


Fig. 26. Deformation-driven microstructural evolution and strain-hardening mechanisms in a dual-phase non-equiatomic FeNiMnCoTiSi CCA showing (a) EBSD maps with FCC (red) and BCC (green) before and after deformation, (b) work hardening rate with true strain indicating dislocation activity, precipitation strengthening, TWIP/TRIP, and grain partitioning, (c) schematics of stages I-V illustrating dislocation dynamics, twinning, and FCC-to-BCC transformation enabling strength-ductility synergy (Courtesy Elsevier and adapted from Ref. [130] with permission No. 6046781028316).

Fig. 29 [100]. These alloys were subjected to various annealing temperatures ranging from 750 °C to 1050 °C. The 3Si and 6Si alloys had pronounced sensitivity to annealing temperature, with lower temperatures (750–850 °C) leading to higher strength but reduced ductility, whereas higher temperatures (950–1050 °C) promote softening, characterized by lower yield and tensile strengths but improved elongation [100]. For the CCA-based compositions, the 6Si had a more favourable strength-ductility balance compared to 3Si, particularly when annealed between 800 and 900 °C, suggesting a beneficial role of increased Si content in stabilizing microstructure and enhancing strain-hardening capacity [42,515]. The addition of Si enhances solid solution strengthening and lowers the stacking fault energy (SFE) [94], promoting TWIP/TRIP effects [42,515] which combines with deformation-induced FCC-to-BCC martensitic transformation in these CCAs/HEAs to yield favourable strength-ductility synergy (Fig. 29) [100]. The AISI 304L which was a reference material, maintains superior ductility across all annealing conditions but poor strength compared to CCAs, showing the potential of 3Si and 6Si as advanced structural materials. Thus, the importance of optimizing thermal treatments to tailor microstructural

features such as grain size, dislocation density, and precipitate distribution with improved strength-ductility synergy.

6.4. Heterostructured microstructures and strength-ductility synergy

Heterostructured microstructures are hierarchical and heterogeneous, with multiple levels of arrangement and complexity of micro-constituents across various length scales. These structures are gaining traction for their strength-ductility synergy in most CCAs/HEAs/MEAs [22,25,115,135,143,144,146,247,248,377,385,553]. The heterogeneous structures composed of zones with markedly different mechanical properties critical for inducing the varying structural properties required for exceptional balance of strength and ductility [377,553]. This surpasses what is typically predicted by the rule of mixtures, a characteristic attributed to the "cocktail effect" of CCAs [133,404].

In CCAs, the microstructural features such as grain boundaries, dislocations, and precipitates – are essential in determining the mechanical, physical, and functional properties. Grains, with their uniform crystalline structures, are separated by grain boundaries that influence strength

Table 12

Non-equiatomic CCAs exhibit tailored grain sizes and mechanical properties, with deformation-induced martensitic transformation enabling TRIP at room temperature [178].

Alloy	Grain size (μm)	UTS (MPa)	Total elongation (%)	Deformation mechanism	Initial microstructure
Deformation-induced FCC $\rightarrow$ HCP martensitic transformation in non-equiatomic Fe-based CCAs/HEAs					
Fe50Mn30Co10Cr10 [203,217]	4.5	~ 870	~ 75	TRIP & TWIP in HCP	FCC + HCP
	6	~ 820	~ 67		
Fe50Mn30Co10Cr10-B (30 ppm) [522]	27	720	~ 49	TWIP/TRIP, TWIP in HCP phase, reverse transformation	
				TWIP/TRIP	
Fe42Mn28Co10Cr15Si5 [519]	–	~ 1150	~ 12		
Fe34Co20Cr20Mn20Ni6 [178]	~ 130	~ 550	~ 45		
Deformation-induced FCC $\rightarrow$ HCP martensitic transformation in non-equiatomic Co-based CCAs/HEAs					
Co35Cr25Mn15Fe10Ni15 [224]	~ 11	~ 810	~ 80	TRIP	FCC
Co45(FeNi)30Cr25 [509]	10.5	841	76		
Co40(FeNi)30Cr25Mo5 [510]	~ 12	~ 990	~ 90		
Co50(FeNi)20Cr25Mo5 [510]	~ 8	~ 1130	~ 60		
Co38Cr33Ni29 [580]	–	~ 840	~ 90		
Co42Cr33Ni25 [580]	–	~ 900	~ 70		
Co50Cr20Ni20Fe5Mn5 [101]	–	~ 1000	~ 50	TRIP/TWIP	
Deformation-induced FCC $\rightarrow$ HCP martensitic transformation in CCAs/HEAs					
Fe45Co35Cr10V10 [178]	4.4	745	70	TRIP	FCC
Fe45Co30Cr10Mn5V10 [581]	9.8	802	66		
Fe46Co30Cr10Mn5V7Si2 [517]	5.1	860	62		
Fe46Co30Cr10Mn5V5Si4 [517]	5.7	962	55		
Fe46Co30Cr10Mn5V2Si7 [520]	2.8	1102	52		
Fe47Co30Cr10Ni5V5Si3 [94]	~ 5	800	84		
Fe47Co30Cr10Ni5V4Si4 [94]	~ 5	903	81		
Fe47Co30Cr10Ni5V2Si6 [94]	~ 5	1128	72		
Fe46Co30Cr10Mn5V2Si7 [517]	6.2	1085	57		FCC + HCP
Fe45Co30Cr10Mn5V2Si8 [178]	7	1099	52		
Fe46Co30Cr10Mn5V2Si7 [520]	10.2	1040	51		FCC + HCP + BCC
Combination of DIMT with other strengthening mechanisms					
Co51Cr25Al8Fe8Ni8 [67]	–	~ 1100	~ 60	TRIP	FCC + NiAl
Fe50Co25Ni12Al8Ti5Mo5	–	~ 1460	~ 23		BCC + FCC + Precipitate
					FCC + Precipitates
Fe49Co21Cr11Mn4Ni4Mo3V2C1Si5 [178]	–	~ 1100	~ 50		
Fe45Co35V10Cr10 [178]	–	~ 1084	~ 45		FCC (Bimodal)
Fe49.5Mn30Co10Cr10Co0.5 [211]	–	~ 1500	~ 15	–	FCC (Bimodal)
Fe39Mn20Co20Cr15Si5Al1 [178,588]	–	~ 1120	~ 52	TWIP/TRIP	FCC + HCP + Precipitate
					FCC (Heterogenous)
Fe40Mn10Co20Cr20Ni10 [108]	–	~ 870	~ 70		

and ductility [93,219]. Defects, including vacancies and dislocations, affect the plastic deformation and thermodynamic behavior of the alloy [9–12,28,553]. Precipitates, formed during the solidification or heat treatment, hinder dislocation movement and thus strengthen the alloy [360–367]. Texture is generally the preferred orientation of grains which contributes to anisotropic properties like strength and conductivity [553]. The interplay between these microstructural features underpins the strength-ductility synergy in CCAs, enabling them to achieve superior mechanical performance [11,12,28,553].

The hierarchical microstructural features (grains, defects, secondary phases, precipitates, and textures), exhibit strain partitioning due to varying stress levels during tensile deformation. This partitioning leads to the accumulation of geometrically necessary dislocations (GNDs) [326,327,346,347,528] and hetero-deformation-induced (HDI) stress-strain effects [93,224,300,377,403]. Additionally, localized chemical heterogeneities create local chemical ordering (LCO) with complex stress-strain fields [93,110,115,219,471], altering dislocation core configurations and sometimes causing short-range dislocation impediments. The complex interactions of dislocations, HDI effects, and other microstructural barriers in CCAs/HEAs enhance work hardening, thereby achieving a strength-ductility synergy [525–527,554,555]. Thus, the strength – ductility synergy is achieved in heterostructure CCAs/HEAs and is better than most conventional dilute and heterogeneous alloys as shown in Fig. 30 [93,219].

The various heterogeneities in CCAs/HEAs are being explored for enhanced structural and functional properties. These structures are mainly associated with nature providing different pathways for

properties synergies rather than trade-offs [224,300,403]. For strength – ductility synergy, complex microstructural architectures such as lamellar (layered) [89,514,584], gradient [21,23,176,226,303,502,528,543,571–573,342,348], multiphase [116,203,514], bimodal [185,211,217,281,300,394] and cellular structures are used to optimize dislocation dynamics and complexities associated with phase interactions [41,93,113,133,151,178,385,450]. These microstructures have distinct structural arrangements in CCAs/HEAs that interacts with dislocation movements, the major carriers of plastic deformation [52,115,215,514,560,562]. This is the mechanism responsible for the synergy in strength and ductility, and other desired and designed structural and functional properties.

6.4.1. Lamellar microstructures

Lamellar microstructures consist of alternating layers or plates of different phases or compositions within the alloy. These structures are typically formed through phase transformations during eutectic solidification or spinodal decomposition [142,191,205,206,248,347,420,482,504,512,513,546,550,584,589]. Generally, the formation of lamellar microstructures is primarily driven by spinodal decomposition [584], where compositional changes occur before any structural transformations. Spinodal decomposition takes place during the undercooling stage, preceding the development of the lamellar structure with schematic is given in Fig. 31 [584]. Lamellar microstructures can significantly enhance the toughness and strength of CCAs or HEAs by providing multiple interfaces that impede crack propagation and dislocation motion. The alternating layers create a composite-like structure

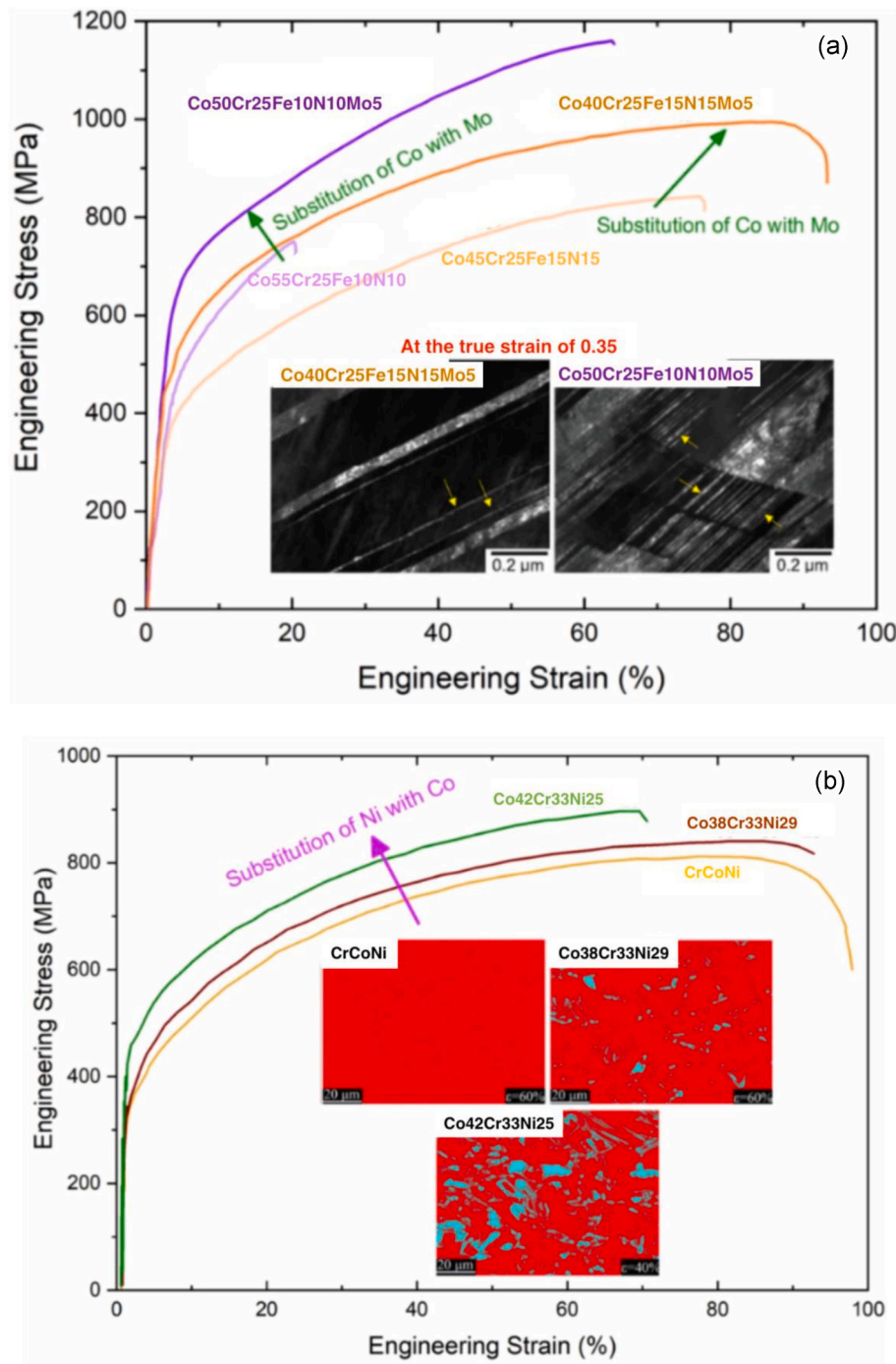


Fig. 27. Influence of alloying elements on the mechanical properties and deformation behavior of TRIP-assisted CCAs/HEAs (a) substitution of Co with Mo (Courtesy of Taylor and Francis and adapted from Ref. [509] under open access license and Elsevier from Ref. [510] with permission No. 6071180596660), (b) Co replacing Ni (Courtesy Elsevier and adapted from Ref. [580] with permission No. 6046790985342) (c) the role of Si in tuning TRIP behaviour in $\text{Fe}_{45}\text{Co}_{30}\text{Cr}_{10}\text{V}_{10}\text{Mn}_{5-x}\text{Si}_x$ and $\text{Fe}_{46}\text{Co}_{30}\text{Cr}_{10}\text{Mn}_5\text{V}_{9-x}\text{Si}_x$ (Courtesy Elsevier and adapted from Ref. [581] with permission No. 6071181081932) and (d) comparison of engineering stress-strain curves at room temperature (RT) and cryogenic temperature (CT) across different Fe-Mn-based CCAs (Courtesy Elsevier and adapted from Refs. [582,583] with permission No. 6046801042588 and 6046801319783).

where each phase can contribute different properties, leading to a more balanced and optimized mechanical performance [142,191,205,206,403,482,513,584,589].

The microstructure of as-cast AlCoCrFeNi2.1 eutectic high entropy alloy (EHEA) showing the nano-lamellar arrangement of L12 (light contrast) and B2 (dark contrast) solid solution phases is given in Fig. 32 [585]. The distinct contrast between the two features, the elemental

mapping and TEM analyses are highlighted in Fig. 32 (b, c, and d). The average grain size was $\sim 100 \mu\text{m}$. These microstructural features are consistent with previous findings with the nanoprecipitation and the hierarchical lamellar microstructure driving the strength-ductility synergy resulting from cryo-rolling with annealing [206]. The nano-lamellar heterogeneous structure effectively accommodates deformation mechanisms providing the strengthening effects, whereas

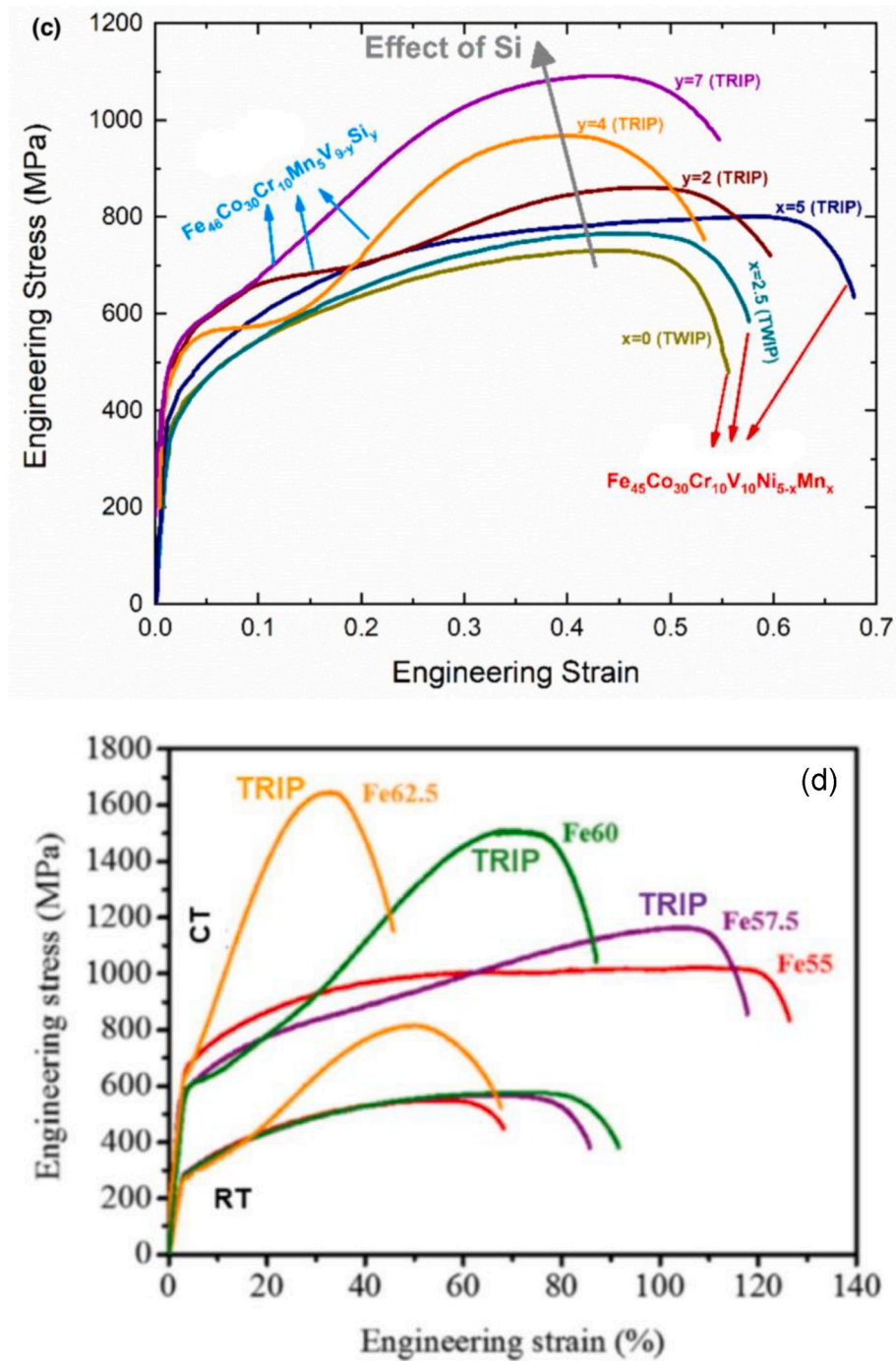


Fig. 27. (continued).

lamellar colonies significantly improved ductility due to the lamellae acting as barriers to crack propagation. A yield strength of ~ 750 MPa, a tensile strength of ~ 1160 MPa and elongation of $\sim 18\%$ were recorded [585]. The unique lamellar arrangement facilitates a more favourable distribution of stress and strain during deformation. The ability to absorb energy and deform plastically before fracture in lamellar structures is crucial for achieving high ductility [88,122,142,403,482,585].

The tensile engineering stress-strain plot of the as-cast AlCoCrFeNi_{2.1} alloy is shown in Fig. 33(a). Compared to other reported EHEAs, the AlCoCrFeNi_{2.1} alloy demonstrated a superior balance of strength and ductility. The fracture morphology in Fig. 33 (b) revealed two distinct features: brittle fracture in the B2 phase with fishbone-like markings, and ductile fracture in the L12 phase, characterized by

necking into sharp lines. The compressive fracture surface in Fig. 33 (d) shows cleavage steps and slip features (in the inset). These indicate a quasi-cleavage fracture in the AlCoCrFeNi_{2.1} EHEA under compression, with micro-cracks initiating in the coarse B2 phase and growing into large cracks after deflecting from the interface. The lamellar structure contributed to the strength – ductility synergy through the Zener pinning effect [248,550,551].

The microstructural characteristics, such as the size and orientation of the lamellae, significantly influence mechanical properties. A eutectoid nano-lamellar microstructure in an Al_{0.3}CoFeNi alloy showed complex interactions between atomic size and chemical ordering [142, 482], ultimately enhancing strength and ductility [142,191,205,206, 482,584,589]. Duplex lamellar B2 and L12 structures were observed in

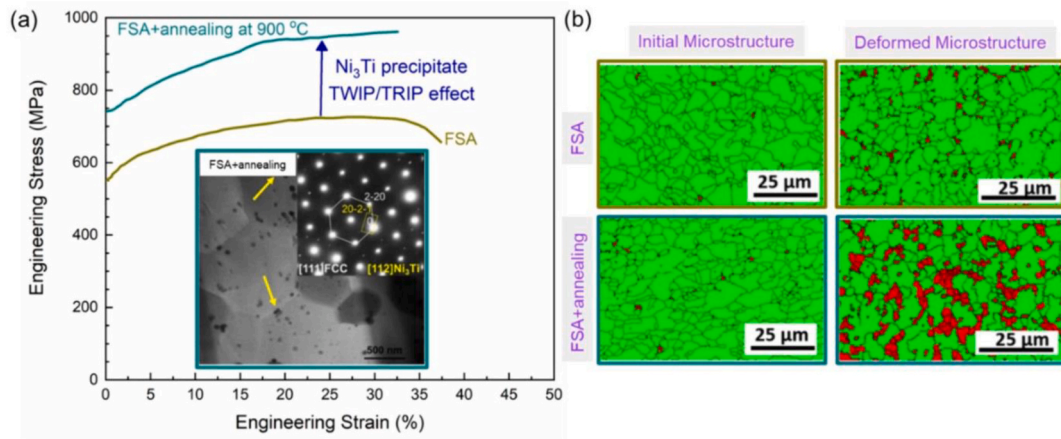


Fig. 28. Enhanced strength and deformation behaviour in FSA-treated alloys via Ni_3Ti precipitation and TWIP/TRIP mechanisms (a) stress-strain response with improved mechanical performance after annealing at 900 °C and (b) the EBSD maps comparing initial and deformed microstructures for FSA and FSA + annealing conditions (Courtesy Nature and adapted from Ref. [16] under Open access license).

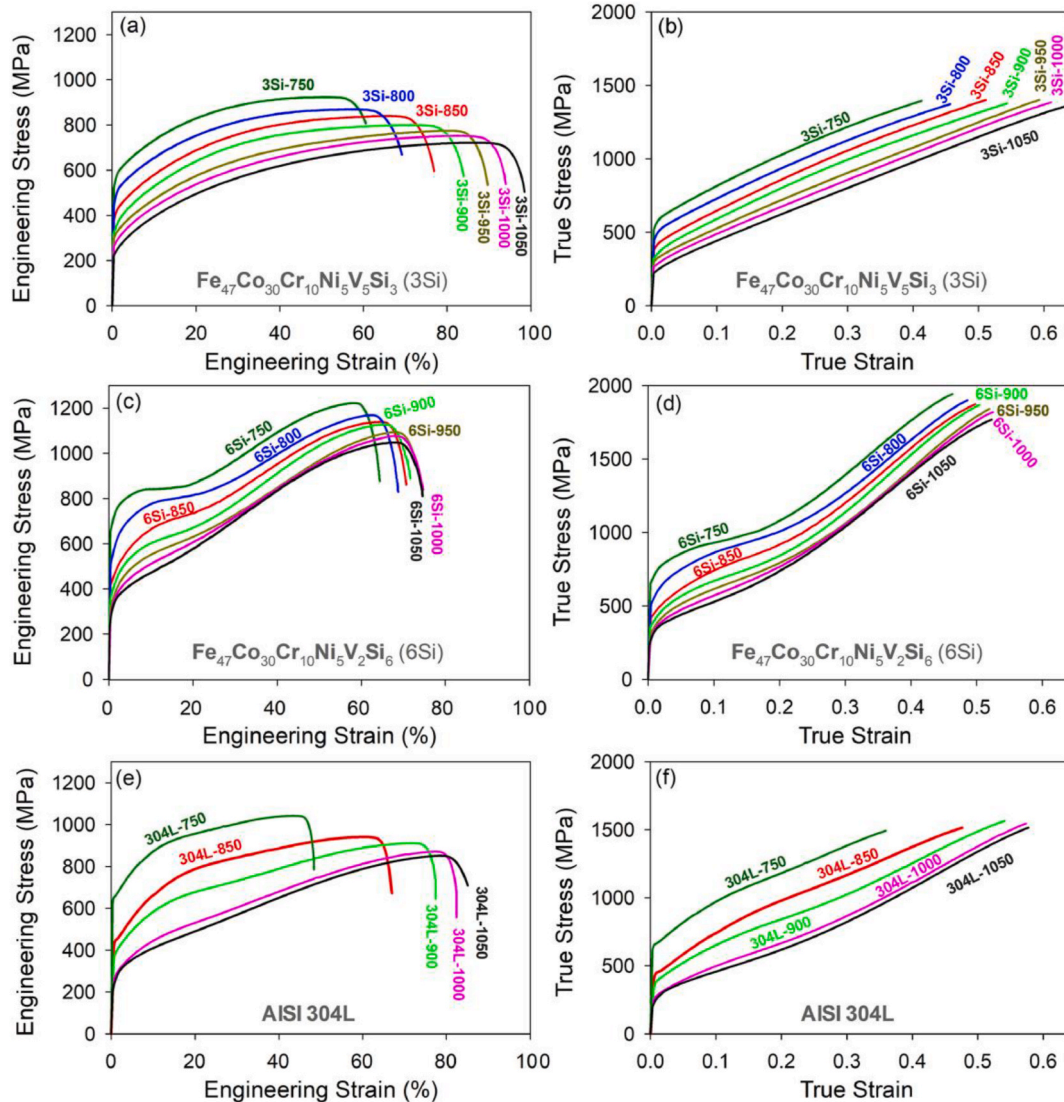


Fig. 29. Engineering and true stress-strain curves of $\text{Fe}_{47}\text{Co}_{30}\text{Cr}_{10}\text{Ni}_5\text{V}_5\text{Si}_3$ (3Si) (a) and (b), $\text{Fe}_{47}\text{Co}_{30}\text{Cr}_{10}\text{Ni}_5\text{V}_2\text{Si}_6$ (6Si) (c) and (d), and AISI 304L (e) and (f) annealed at different temperatures (750–1050 °C), illustrating the effect of thermal processing on strength and ductility (Courtesy Elsevier and adapted from Ref. [100] with permission No. 6046830655123).

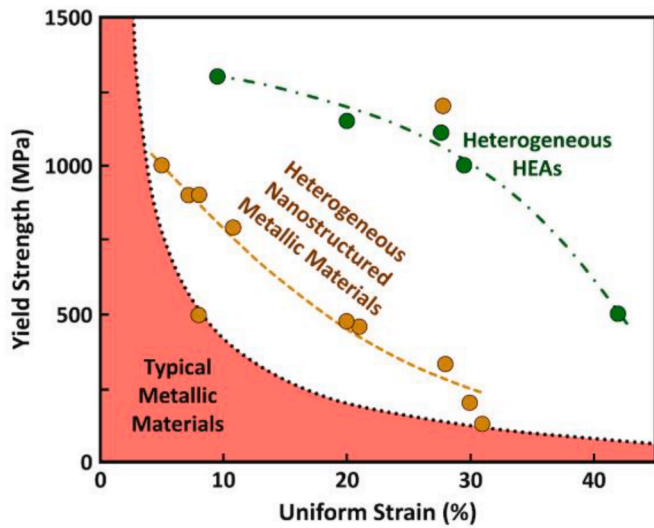


Fig. 30. Typical strength – ductility behaviour of conventional metallic materials, heterogeneous nanostructured metals and heterogeneous CCAs/HEAs (Courtesy Elsevier and adapted from Ref. [93] with permission No. 6046820710702 and Courtesy Nature and adapted from Ref. [219] under Open Access license).

CoCrFeNiNb0.5–0.8, FeNiCoAl [36,248,301,522,550,551,586], FeNiCoAlCrB [248,550,551] and AlCoCrFeNi [206,221,429] with strength ranging between 800 and 1600 MPa and elongation ranging between 14 and 40 [206,221,248,429,550,551,587]. Thus, by optimizing lamellar sizes with some martensitic transformation coupled with solid solution, interface and precipitate strengthening leads to enhanced strength-ductility synergy [102,248,550,551]. These microstructural features are driven by the thermomechanical treatment processes [206, 221,429,587].

6.4.2. Gradient microstructures

Gradient microstructures involve a continuous change in composition or phase distribution across a material. This type of microstructure

is often engineered to create a gradual transition in properties, such as hardness or toughness, from one region of the material to another. In CCAs or HEAs, gradient microstructures can be used to optimize performance by tailoring the properties locally to withstand specific stresses or environmental conditions. This gradual variation in microstructure can improve the overall performance of the material by reducing stress concentrations and enhancing resistance to crack propagation.

Gradient microstructures play a pivotal role in enhancing the strength-ductility synergy in HEAs/CCAs through multiple mechanisms. This is summarized in Table 13. Hetero-Deformation-Induced (HDI) hardening, driven by variations in grain size, nano-twins, and dislocation densities, contributes significantly to increased strength while maintaining ductility [190,225,503]. Additionally, the combination of deformation twinning and dislocation slip within gradient hierarchical structures enhances strain hardening [225,589], enabling simultaneous improvements in both strength and plasticity. Phase architecting, particularly in dual-phase HEAs with FCC and BCC microstructures [309,341,362,504,512,540], supports strain hardening by buffering dislocations at heterogeneous phase boundaries. This provides the pathway for multiscale strengthening mechanisms [388].

The multiscale strengthening is achievable by creating hierarchical microstructures leveraging gradients in composition, grain size and defect typology. This is schematically shown in Fig. 34 where gradient in composition and SFE are tailored to develop heterogeneous microstructure for strength-ductility synergy [388,456]. Near one end of the gradient, localized short-range ordered solute clusters, ordered precipitates, and dislocation entanglements boost strength by impeding slip. Farther along the gradient, low SFE regions foster stacking faults and mechanical twinning (both primary and secondary), which accommodate large plastic strain and thereby enhance ductility. Slip-induced microbands add another layer of heterogeneity [88,122], with non-uniformly distributed deformations in the alloy. Thus, these defects such as precipitates, twins, dislocation structures, and stacking faults create a tailored balance between strength and ductility. In essence, the spatial variation of composition and SFE promotes different deformation mechanisms in different regions, achieving a synergistic response under loading.

The development of gradient microstructures depends on the manufacturing method, including surface mechanical grinding

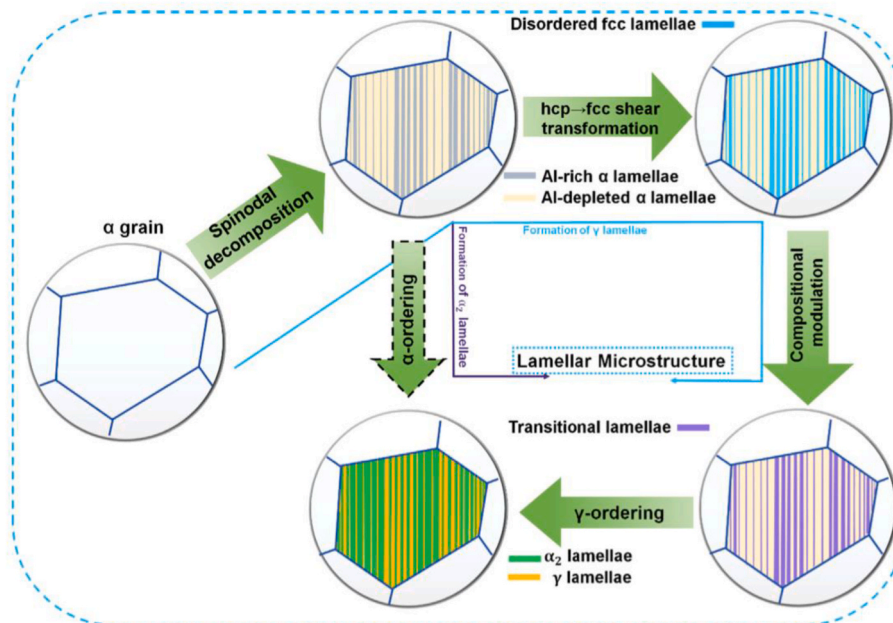


Fig. 31. Schematics showing the different stages and processes of lamellar microstructure formation (Courtesy Elsevier and adapted from Ref. [584] under Open Access license).

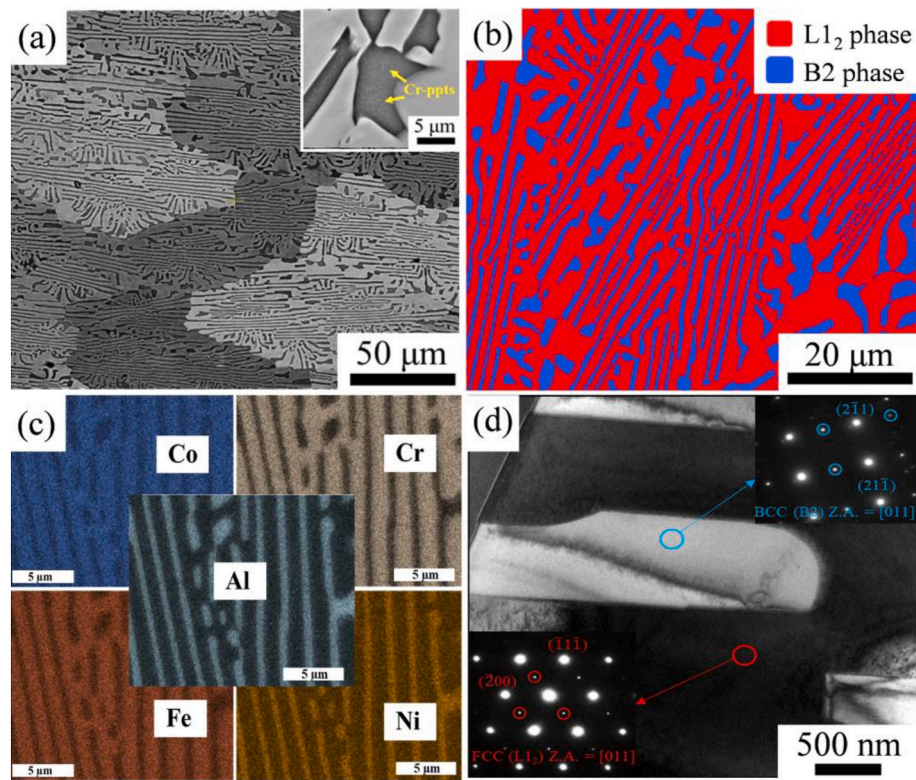


Fig. 32. Eutectic lamellar structure of as-cast AlCoCrFeNi2.1 showing (a) back scattered electron diffraction mode, (b) typical EBSD map showing the lamellar structure of L12 and B2 phases, (c) EDS elemental mapping and (d) TEM bright field confirming the lamellar structure (Courtesy Nature and adapted from Ref. [585] under Open Access license).

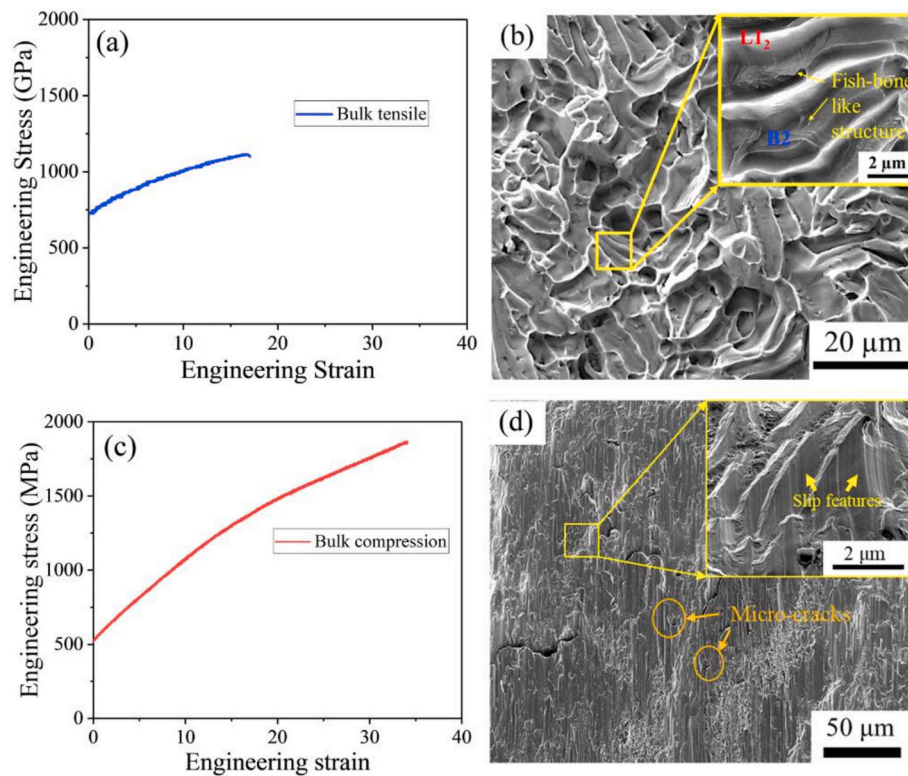


Fig. 33. Stress – strain curves ((a) and (c)) and fractured surfaces ((b) and (d)) of AlCoCrFeNi2.1 alloys (Courtesy Nature and adapted from Ref. [585] under Open Access license).

Table 13

The mechanisms associated with gradient microstructure and their contributions to strength-ductility synergy.

Mechanisms	Contributions to strength-ductility synergy
Dislocation and segregation	Strength-ductility by gradient or cellular sizes of grains and segregation [190,309,341,503,504,589,590]
Phase composition	Heat treatment (annealing) alters phase distribution for synergy [190,503,542,544,589]
Dislocation density	High dislocation densities influence cyclic hardening and softening
Nanostructure manipulation	Development of gyroid nanostructures affect strain softening

treatment (SMGT), surface mechanical rolling treatment (SMRT), surface mechanical attrition treatment (SMAT) [145,340,422] and rotationally accelerated shot peening (RASP) [225]. These techniques typically produce thin nanostructured layers (~200 μm thick), while high-pressure torsion enables large-scale gradient structures [589].

Surface treatments like USRP and LSP enhance the effect by introducing sub-grains, dislocations, and nano-twins, stabilizing plastic deformation and delaying necking [190,503,589,590]. This effectively mitigates the strength-ductility trade-off [225,309,503,504,544,589], making the alloys ideal for high-performance applications.

6.4.3. Cellular microstructures

Cellular microstructures are characterized by a network of cells or grains with distinct boundaries. These cells often form during solidification processes, where solute partitioning and rapid cooling lead to the development of a cellular pattern. The cell boundaries typically act as barriers to dislocation movement, enhancing the strength of the alloy. The maximization of the configurational entropy and enthalpy of mixing stabilizes simple solid solution phases such as FCC, BCC and HCP structures [9–11,103,177,187,214,233,234,240,263,405–407,448]. This allows for the cellular microstructures during directional solidification process, where the temperature gradient promotes the development of these cellular and dendritic structures [115,169,177,225,390,

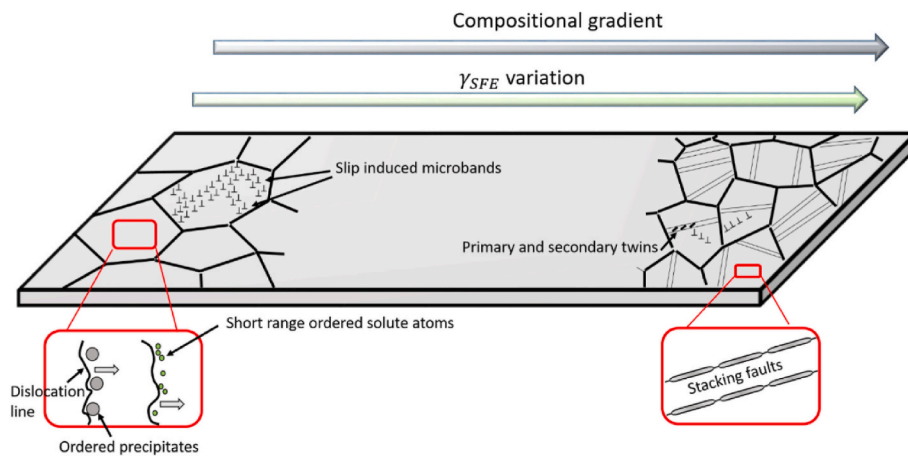


Fig. 34. Schematic illustrating how a gradient microstructure with spatial variations in SFE and compositional order promotes heterogeneous deformation mechanisms (precipitates, dislocations, and twins) to synergistically enhance both strength and ductility (Courtesy of Elsevier and adapted from Ref. [388] under open access license).

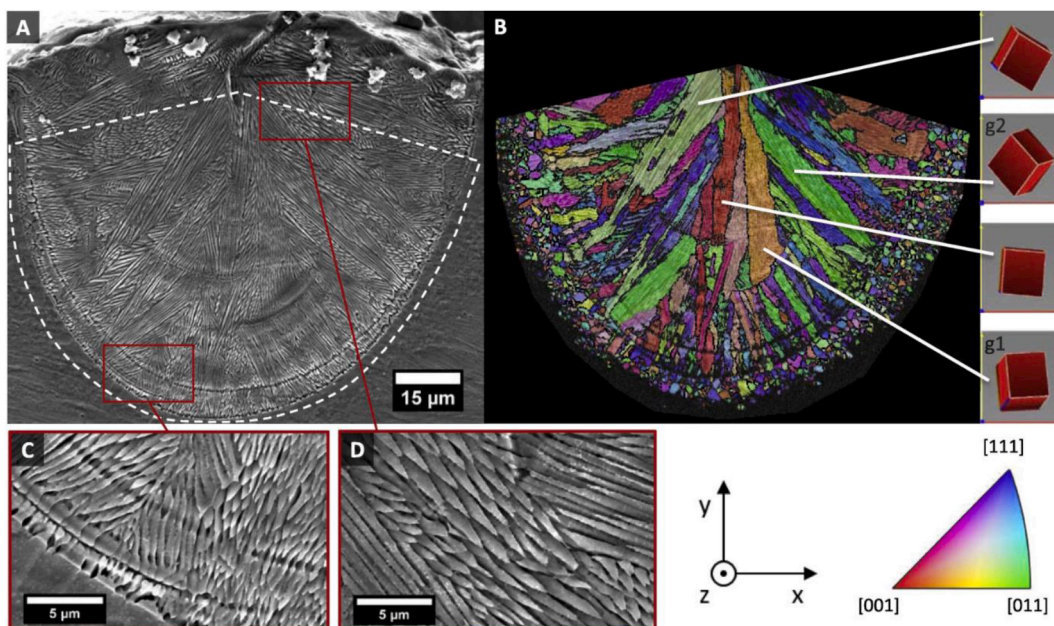


Fig. 35. Typical cellular microstructure of CrCoFeMnNi produced by additive manufacturing with (a) EBSD, (b) single-track cross-section in a single-layer build, (c) and (d) high magnified cellular morphology (Courtesy of Elsevier and adapted from Ref. [586] under Open Access license).

410]. These cellular structures provide pathways for dislocation movement [205,443,563,586,589] which is essential for ductility and simultaneously contributing to strength through solid solution hardening mechanisms.

The different dislocation pathways and their interactions with the complex cellular microstructures is a template for strength-ductility synergy. The interactions between dislocations, slip, stacking faults and nanotwins are critical mechanisms [93,219,343,408–411,413,414,535,564]. During deformations, dislocation-slip is prevalent in fine grains, while stacking faults and nanotwins are activated in ultrafine grains, leading to strain partition and hetero-deformation-induced (HDI) stress accumulation via pileups of massive dislocations at grain boundaries and domain boundaries, resulting in significant HDI hardening [43,93,102,113,219,377,423,514,538].

The 3D printing approach is used to fabricate Cantor-based alloys with the characteristic cellular microstructures. Fig. 35 shows a laser powder bed fusion printed cellular microstructure of CrCoFeMnNi SEM with the EBSD IPF-y map of a single-track cross-section in a single-layer build [586]. The high cooling rate from local melting on a cold substrate resulted in fine cells within the melt pool (Fig. 35(c) and (d)), with cell spacings ranging from 0.52 μm to 0.64 μm , averaging 0.59 μm . These finer cells, contribute to higher hardness by restricting dislocation movement [48,586]. Fig. 35(a) shows cells growing epitaxially from the substrate, aligned with one of their $\langle 001 \rangle$ orientations normal to the fusion line, driven by the thermal gradient. Grain competition during solidification favoured grains like g1, better aligned with the heat flux, over others such as g2 (Fig. 35 (b)) [305,586].

The cellular microstructure in CCAs/HEAs enhances strength-ductility synergy through several mechanisms. Phase interface strengthening delays crack propagation in directionally solidified eutectic HEAs (DSHEAs) with L12 and B2 phases [257,377,581]. Microstructural refinement increases fracture strain more than 40 % without compromising strength in most alloys [190,371]. Hierarchical microstructures and dislocation networks induced by laser powder bed fusion improve mechanical performance in CoCrNi [126,189,214,322]. Furthermore, sequential phase transformations involving Shockley dislocations and reverse transformations to FCC nanotwins create

heterogeneous microstructures enhancing ductility and strength [257,377,581,586].

6.4.4. Bimodal, trimodal and multiphase microstructures

Bimodal and trimodal microstructures play a pivotal role in enhancing strength-ductility synergy in CCAs/HEAs. This is achievable through various mechanisms [185,211,217,281,300,394,408,409,423] – heterogeneous deformation induced by different grain sizes and phases in CoCrFeNiMn HEA [591], enhances strain hardening and delays fracture, achieving high strength (~ 1 GPa) and good ductility (12 %) [398,538]. Trimodal microstructures facilitate the sequential activation of deformation mechanisms like TRIP and TWIP [185,211,217,281,300,394], leading to multi-stage work hardening that significantly improves ductility while maintaining strength. Additionally, boundary strengthening through bimodal microstructures and nanotwins, as observed in the FCC phase of AlCoCrFeNi eutectic alloy, contributes to strength-ductility synergy [24,118,138,193]. Multi-scale reinforcements, including micro-scale Laves phases, nano-scale precipitates, and atomic-scale short-range order structures, further contributed to high yield and tensile strengths without compromising ductility [143,359,408,409,423].

Bimodal and trimodal grain size distributions [185,211,217,281,300,394,538,578,579], achieved through processes such as high-pressure torsion [135,149,150], cold rolling [21,124,145,342,422], equal channel angular pressing (ECAP) [587] and annealing [135,149,150]. This significantly improves the strength and ductility of CCAs like CrCoNi [135,149,150] and CoCrFeNiAl_{0.1} [220]. The combination of ultrafine, fine, and coarse grains creates hard and soft zones, facilitating strain hardening through the generation of geometrically necessary dislocations (GNDs) at grain boundaries [185,211,217,220,281,300,394,538,578,579]. These grain structures also induce stress partitioning and concentration at the interfaces during plastic deformation, raising the local stress to the critical resolved shear stress (CRSS) required for twinning [211,217,220,281,300,394,564–567]. This stress activation promotes twinning, leading to enhanced strain hardening and the synergy between strength and ductility, with strengths reaching ~ 1.5 GPa and ductility of ~ 30 % [135,149,150]. A multimodal grain

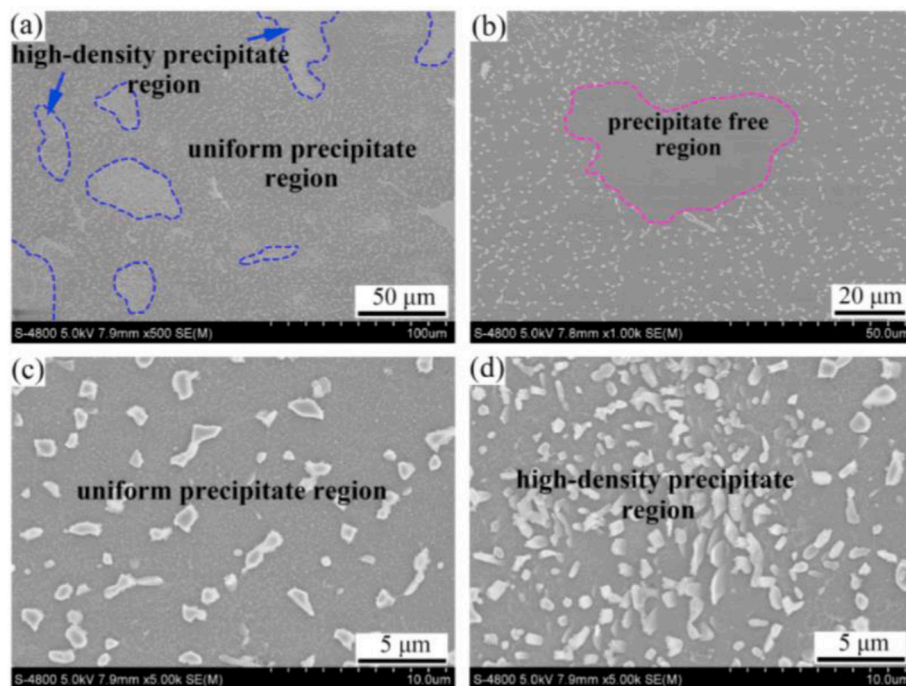


Fig. 36. Multimodal microstructure of an AZ91 ECAP alloy showing (a) SEM image at low magnification with high density and uniform precipitates, (b) precipitate free regions and (c) and (d) magnified precipitates (Courtesy of MDPI and adapted from Ref. [587] under Open Access license).

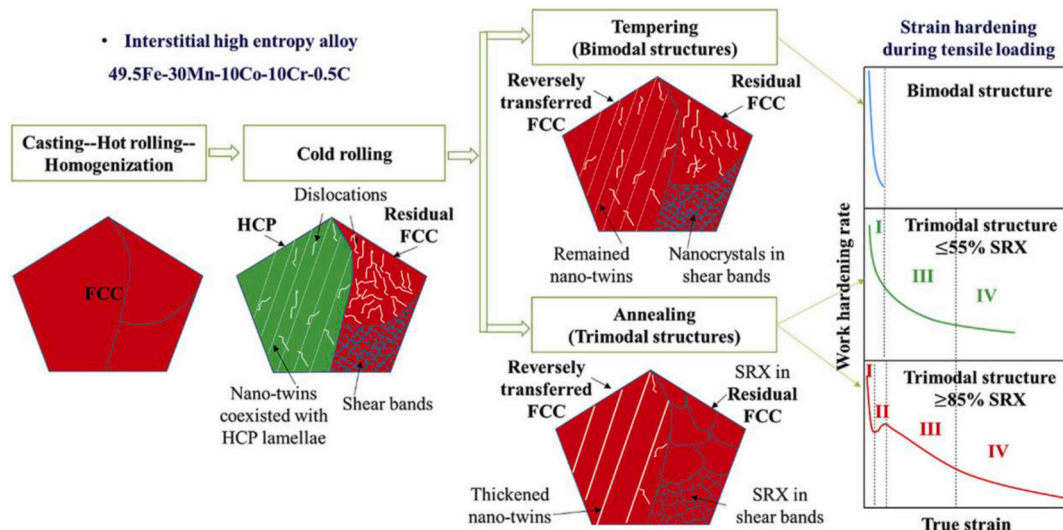


Fig. 37. Schematics of postprocessing of interstitial FeMnCoCrC with bimodal and trimodal microstructures driven by phase transformation (Courtesy of Elsevier and adapted from Ref. [211] with permission No. 6047411316319).

Table 14

Effects of bimodal and trimodal microstructural features on mechanical properties of CCAs.

Mechanical property	Bimodal and trimodal microstructure effects
Yield strength	Up to ~1300 MPa [17,18,123,185,211,217,281,300,394,446,481,519,566,588]
Ductility	>26 % [113,141,143,145,281,408,415,592–594]
Hardness	Extremely higher than monomodal microstructures [591].
Compressive yield strength	Above 1600 MPa at room temperature
Tensile strength	Exceeding 1800 MPa [17,18,123,185,211,217,281,300,481,519,566,588,394,446]

structure with a mix of coarse and fine grains was formed in the AZ91 alloy after an ECAP processing (Fig. 36). Subsequent short-time aging led to an increase in the volume fraction of fine grains due to static recrystallization, along with a slight growth in their size. Thus, strength-ductility synergy was realized.

Hierarchical microstructures are created by thermomechanical processing for enhanced mechanical properties. The schematic in Fig. 37 shows the creation of hierarchical microstructures via homogenization, cold rolling, and tempering/annealing [185,211,217,281,300,394]. Initially, the Fe49.5Mn30Co10Cr10C0.5 alloy had an equiaxed FCC microstructure, and cold rolling induced HCP-martensite within the FCC matrix, forming a dual-phase structure with severe shear bands at 67 % deformation (true strain 1.1). Heat treatment at 400 °C reversed the HCP-martensite to FCC, forming twins in the parent grains, while short tempering promoted recovery in large grains and preserved nano-grains near shear bands, resulting in a bimodal structure. During annealing, static recrystallization, driven by the deformation and dislocation density of shear bands led to finer grains in the shear bands, while residual FCC grains developed dense dislocation walls, similar to other FCC metals under large strain. The typical effects of these microstructural features (bimodal or trimodal) on mechanical properties are presented in Table 14.

The application of alloy design and thermomechanical heat treatment was used to induce strength-ductility synergy in modified FeMn-CoCrC with Al. A minor Al addition in Fe39Mn20Co20Cr15Si5Al1 HEA, processed by FSP and annealed at 650 °C, unexpectedly stabilized the FCC phase due to Al-rich precipitation reducing matrix Al content. This enabled reverse transformation and refined microstructure (Fig. 38)

[587], enhancing mechanical performance with a UTS of ~1.12 GPa and ~52 % elongation, overcoming the strength–ductility trade-off.

Producing a bimodal microstructure is an effective strategy to overcome the strength–ductility trade-off in most advanced structural metals. Multiple heat treatment stages such as cold rolling followed by post-deformation annealing above the reversion temperature (~750 °C) enable the formation of refined and coarse grains (Fig. 39) [139]. This thermal pathway stabilizes a bimodal structure, significantly enhancing strength (~970 MPa) while retaining good ductility (~45 %), offering a simpler alternative to severe plastic deformation techniques.

6.5. Analytical model for strength-ductility trade-off

A dislocation-based model offers predictive insight into the strength–ductility trade-off. This is schematically shown in Fig. 40 where shear-induced plasticity in a confined polycrystalline material [186]. Fig. 40(a) illustrates dislocation motion within individual grains under applied shear stress, where dislocations glide along slip planes and accumulate at grain boundaries acting as barriers [186,360–367,564–567]. This accumulation generates local stress concentrations, potentially activating additional slip systems or grain boundary-mediated deformation [186,564–567]. Furthermore, Fig. 40 (b) shows the resulting macroscopic deformation formed by the cumulative lateral displacement of grains due to intragranular slip with a staircase-like shear profile [186,360–367]. Generally, the various models associated with strength–ductility behaviour of metals provide quantitative framework quantifying the inverse correlation between strength and ductility through series of grain – size – dependent equations. These models which are derived from dislocation pile – up mechanisms (Fig. 40) and based on continuous dislocation theories [595,596] are given as Equations (14)–(21) [186].

$$E_c = \frac{1-\nu}{2\mu} \left[(\tau_c - \tau_0) \sqrt{\frac{\pi D}{2}} \right]^2 \quad (14a)$$

$$\tau_c = \tau_0 + \sqrt{\frac{4\mu E_c}{\pi(1-\nu)}} D^{-1/2} \quad (15a)$$

$$u(x) = \frac{2(1-\nu)(\tau_c - \tau_0) \left(\sqrt{\left(\frac{D}{2}\right)^2 - x^2} \right)}{\mu} \quad (16)$$

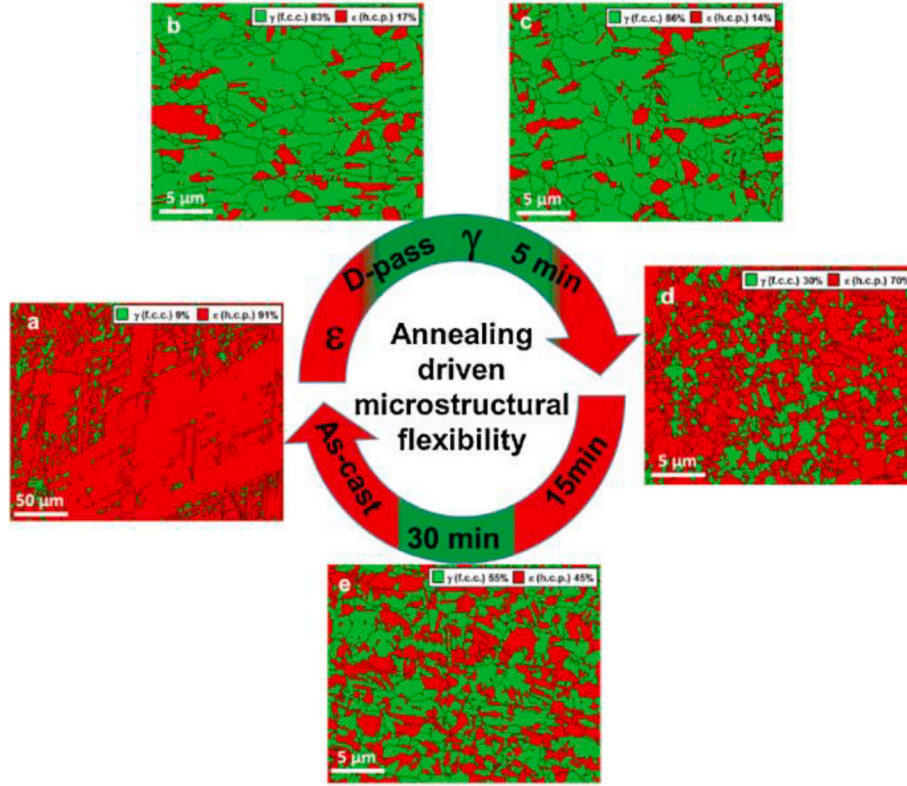


Fig. 38. Annealing-driven microstructural flexibility in Fe-based HEA enables controlled FCC (γ) to HCP (ϵ) phase transformation through FSP and 650 °C annealing, allowing tunable strength–ductility balance (Courtesy of Elsevier and adapted from Ref. [587] with permission No. 6047420429474).

The equations describe the interplay between grain size, dislocation glide resistance, and interfacial strength (Equations (14)–(21)). This shows that increasing strength through conventional approaches such as refinement does compromise ductility. Thus, highlights the need for alternative strategies to break the trade-off. Mechanistically, the trade-off model hinges on the balance between dislocation accumulation and interfacial failure. As dislocations pile up against grain boundaries, they induce localized stress concentrations that can initiate micro-cracking, particularly when grain size is reduced. The model reveals that shear stress increases with reduced grain size (as per Hall–Petch), but this comes at the cost of diminished plastic strain. It underscores the inherent challenge: refining microstructure boosts strength but truncates the dislocation glide length necessary for ductility.

$$\bar{u} = \frac{1}{D} \int_{-D/2}^{D/2} u(x) dx = \frac{\pi(1-\nu)(\tau_c - \tau_0)D}{4\mu} \quad (17)$$

$$\gamma_c = \gamma_0 + \frac{1}{D} = \gamma_0 + \frac{\bar{u}}{H_c} = \gamma_0 + \frac{\pi(1-\nu)(\tau_c - \tau_0)D}{4\mu H_c} \quad (18)$$

$$\gamma_c = \gamma_0 + \sqrt{\frac{\pi(1-\nu)E_c}{4\mu H_c^2}} D^{-1/2} \quad (19)$$

$$\text{UTS} : \sigma_b = \sigma_0 + M \sqrt{\frac{4\mu E_c}{\pi(1-\nu)}} D^{-1/2} \quad (20)$$

$$\text{UE} : \epsilon_u = \epsilon_0 + \frac{1}{M} \sqrt{\frac{\pi(1-\nu)E_c}{4\mu H_c^2}} D^{-1/2} \quad (21)$$

To overcome this, materials must employ supplementary mechanisms such as promoting dislocation cross-slip, enhancing interface strength, or enabling distributed strain via twinning (TWIP) or

transformation-induced plasticity (TRIP). High-entropy and complex concentrated alloys benefit from such mechanisms, particularly via engineered heterogeneities that introduce back-stress [348,422–424, 523] and GND accumulation [326,327,346,347,528]. Thus, this analytical model not only explains the observed strength–ductility inverse correlation but also rationalizes why certain alloy design strategies especially those leveraging dislocation architecture can transcend the traditional trade-off.

7. Comparison of strength–ductility trends in conventional alloys and CCAs/HEAs

The strength–ductility synergy of conventional alloys and CCAs/HEAs have been initially compared based on crystal structures as given in Fig. 41 [199]. Although, most of the first generation of CCAs/HEAs designed were not fully optimized from compositional and microstructural standpoint, there were some comparable trends with advanced conventional alloys such as first, second and third advanced high-strength steels (AHSS) based on crystal structures. This is shown for FCC and FCC1 + FCC2 CCAs/HEAs in Fig. 41(a) with excellent ductility but with moderate strength below 1000 MPa comparable to austenitic stainless steels and Al-based alloys. Fig. 41 (b) shows BCC and BCC1+BCC2 CCAs/HEAs, which offer significantly higher tensile strengths (up to ~2000 MPa) but often at the expense of ductility, aligning with martensitic and 3rd generation AHSS. In Fig. 41 (c), the FCC + BCC dual-phase CCAs/HEAs show promising strength–ductility synergy due to effective strain hardening and phase synergy, comparable to dual-phase steels and TRIP steels [199]. Finally, Fig. 41 (d) shows FCC + HCP and BCC + HCP CCAs/HEAs occupying a region of moderate ductility and high strength, illustrating the potential of HCP-containing microstructures to enhance strength while maintaining reasonable formability.

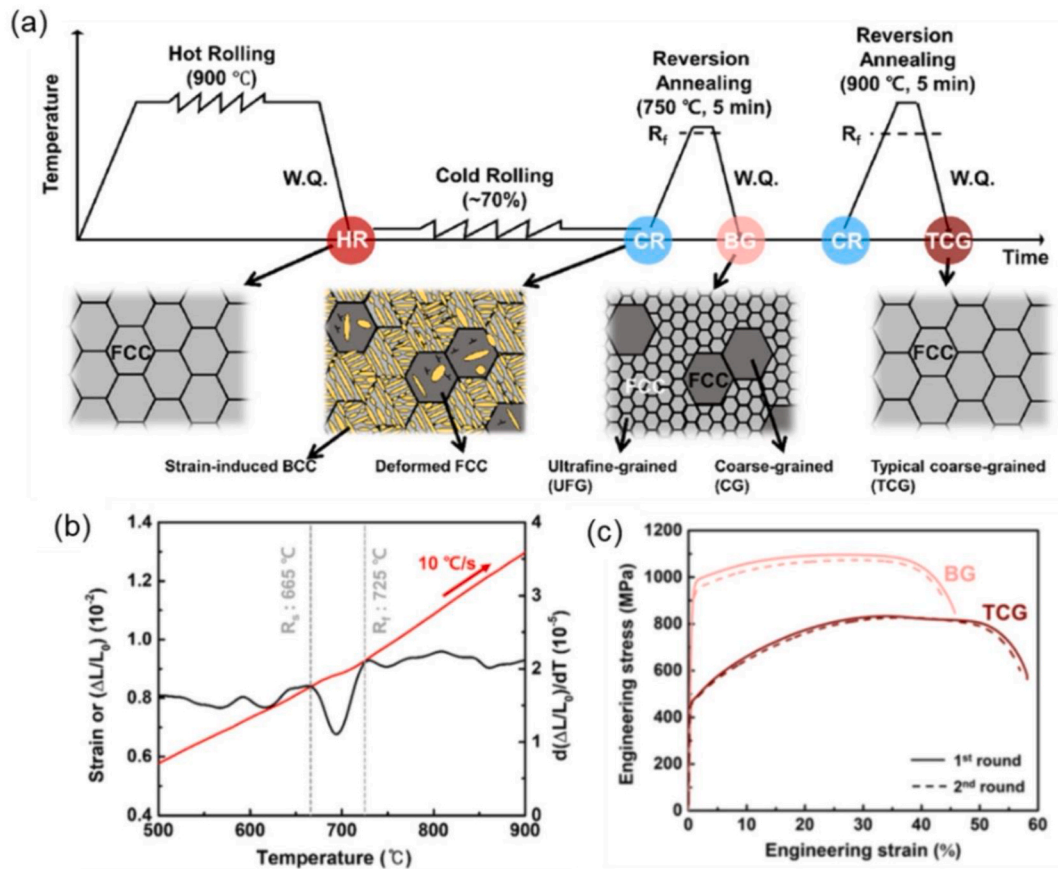


Fig. 39. Schematic showing (a) fabrication process of a bimodal structure (b) strain – temperature plot for the reversion temperature determination and (c) engineering stress–strain curves under two different conditions: one with a bimodal grain structure and the other with a fully recrystallized structure featuring a grain size of 5 μm (Courtesy of Elsevier and adapted from Ref. [139] with permission No. 6047420834548).

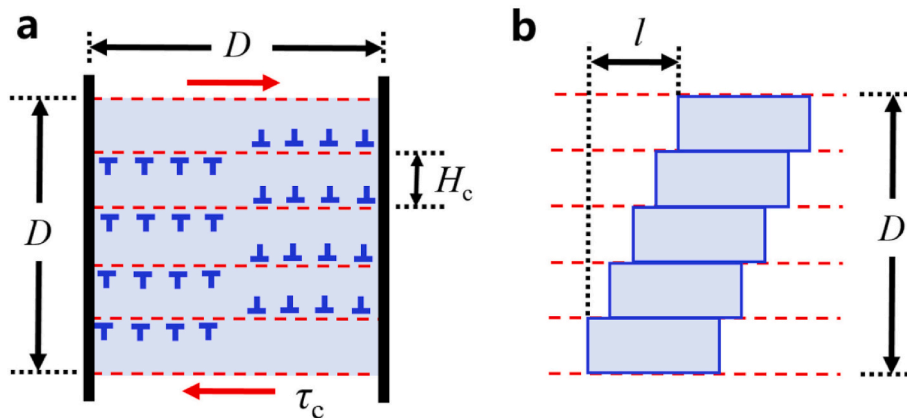


Fig. 40. Modeling the strength – ductility trade-off based on the schematic showing (a) dislocation slip in a confined polycrystalline material under shear stress, with dislocations gliding within grains of height H_c and accumulating at grain boundaries. (b) Resulting shear deformation, where each grain undergoes a lateral shift ' l ', forming a staircase-like profile across the total height D (Courtesy Elsevier and adapted from Ref. [186] with permission No. 6061790538807).

Superior strength–ductility synergy is observed in CCAs/HEAs upon microstructural engineering resulting from dynamic deformation mechanisms. A comparative plot of total elongation versus tensile strength for a variety of structural metallic materials, including steels, high-entropy alloys (HEAs), and conventional alloys are given in Fig. 42 [178]. The BCC-TRIP CCAs/HEAs and Co-rich TRIP CCAs/HEAs showed exceptional strength – ductility synergy, surpassing conventional FCC HEAs, dual-phase steels, and martensitic steels. The BCC-TRIP CCAs/HEAs maintained tensile strengths above 1000 MPa with elongations

exceeding 40 %. Thus, these alloys are promising candidates for advanced structural applications. Traditional materials such as ferritic stainless steels and Al or Mg alloys had limited strength-ductility, emphasizing the superior performance window of the CCAs/HEAs systems. By exploring the combined effects of conventional strengthening and toughening mechanisms with complex alloying strategies, outstanding combination of properties are possible for designing the next-generation structural and functional materials.

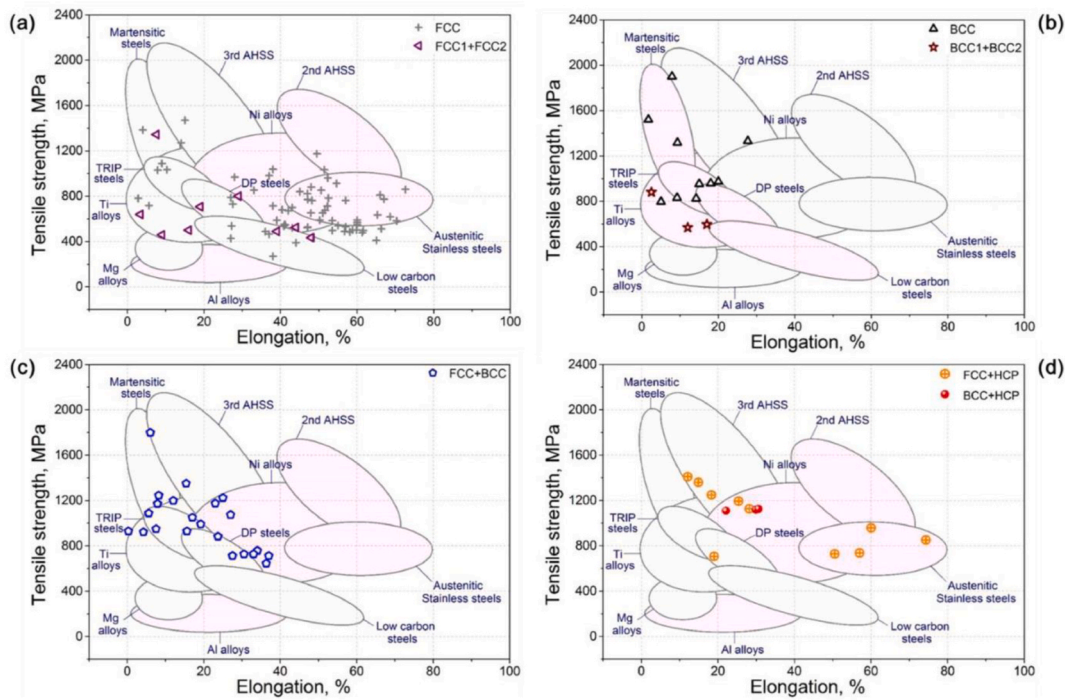


Fig. 41. Compared with conventional alloys, multi-phase CCAs showed strength–ductility synergy of HEAs/MEAs categorized by phase composition with (a) FCC/FCC2, (b) BCC/BCC2, (c) FCC + BCC, and (d) FCC/BCC + HCP (Courtesy Elsevier and adapted from Ref. [199] with permission No. 6047421406708).

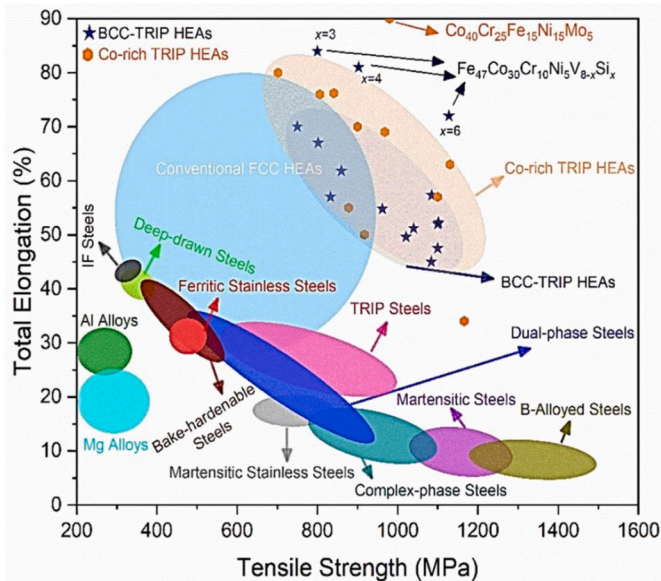


Fig. 42. Comparison of the strength – ductility synergy of CCAs/HEAs with the conventional dilute alloys (Courtesy Elsevier and adapted [178] with permission No. 6047430398484).

8. Perspectives on areas for future research direction

Recent advancements in CCAs/HEAs have highlighted several underexplored mechanisms that could further enhance their mechanical performance. Notably, chemical short-range order (CSRO) has been identified as a significant factor influencing strength–ductility synergy. The CSRO refers to the non-random distribution of atoms over short distances, which can affect dislocation movement and, consequently, mechanical properties. Additionally, the role of interstitial elements, such as carbon and nitrogen, in modifying phase stability and enhancing

mechanical properties has garnered attention. These interstitials can lead to the formation of complex precipitates and influence the stacking fault energy, thereby affecting deformation mechanisms like twinning and phase transformation. Despite these insights, the precise control and understanding of these mechanisms remain uncharted areas for further investigation.

Emerging alloy systems, particularly those incorporating lightweight elements, present promising avenues for research. For instance, aluminum-containing refractory CCAs/HEAs have demonstrated impressive mechanical properties, including high compressive yield strengths and significant ductility, making them suitable for high-temperature applications. Similarly, the exploration of medium entropy alloys (MEAs) with tailored compositions offers the potential to achieve desirable mechanical properties while simplifying the alloy design process. These systems require comprehensive studies to fully understand their phase stability, deformation mechanisms, and potential applications.

Advancements in experimental techniques and modeling tools are pivotal in unraveling the complex behaviors of CCAs and HEAs. In-situ characterization methods, such as high-energy X-ray diffraction and transmission electron microscopy, enable real-time observation of microstructural evolution during deformation. Coupled with computational approaches like the CALPHAD method and machine learning algorithms, researchers can predict phase formations and mechanical behaviors with greater accuracy. These integrated methodologies facilitate a more profound understanding of the interplay between composition, processing, and properties, thereby accelerating the development of alloys with optimized performance.

There is an emphasis on the importance of interdisciplinary approaches to advance CCA and HEA research. The integration of artificial intelligence (AI) and machine learning (ML) in alloy design has been highlighted as a transformative strategy. By leveraging vast datasets and predictive models, AI and ML can identify optimal compositions and processing parameters more efficiently than traditional methods. Furthermore, the adoption of sustainable practices, such as the use of environmentally benign elements and energy-efficient processing

techniques, aligns with global efforts to reduce the environmental impact of material production. Additive manufacturing offers the potential to fabricate complex geometries and tailor microstructures, thereby expanding the application scope of CCAs and HEAs.

Funding and international collaborations play a crucial role in shaping the research landscape of CCAs and HEAs. Countries like China, the United States, and Germany have been at the forefront, investing in large-scale research initiatives and fostering collaborations among academia, industry, and government institutions. These partnerships facilitate the sharing of resources, expertise, and data, thereby accelerating innovation and addressing complex challenges in alloy development. Moreover, open-access databases and collaborative platforms enhance transparency and reproducibility, essential factors for the progress of scientific community.

To overcome current limitations and unlock the full potential of CCAs and HEAs, future research should focus on several strategic areas. Developing scalable and reproducible processing techniques is essential for transitioning from laboratory-scale experiments to industrial applications. Enhancing the mechanistic understanding of deformation behaviours through advanced characterization and modeling will enable the design of alloys with tailored properties. Integrating AI and ML tools can expedite the discovery and optimization of new alloy systems. Emphasizing sustainability and environmental considerations in alloy design aligns with global priorities and ensures the long-term viability of these materials.

The field of CCAs/HEAs is poised for significant advancements through the exploration of underutilized mechanisms, innovative alloy systems, and interdisciplinary methodologies. By addressing existing challenges and embracing collaborative, data-driven approaches, high-performance materials can be developed meeting the demanding requirements of modern engineering applications. The integration of sustainability, scalability, and advanced modeling tools will be instrumental in transitioning these novel alloys from research laboratories to real-world applications, thereby revolutionizing the landscape of structural materials.

9. Summary and concluding remarks

The strength–ductility trade-off has long constrained the performance of structural metals necessitating compromises in either strength or ductility. This review critically evaluated the emergence of Complex Concentrated Alloys (CCAs) and High Entropy Alloys (HEAs) as transformative solutions to this longstanding challenge. It has highlighted the unique compositional strategies, microstructural engineering techniques, and synergistic deformation mechanisms such as twinning-induced plasticity (TWIP), transformation-induced plasticity (TRIP), and back-stress strengthening that collectively drive exceptional mechanical performance. Material systems like CrCoFeMnNi, AlCoCr-FeNi_{2.1}, and CoCrNi-based alloys demonstrated how careful tuning of stacking fault energy, grain refinement, interstitial additions, and nanoprecipitate distribution can achieve unprecedented combinations of strength and ductility, surpassing those of conventional alloys.

Bibliometric analysis further revealed the exponential growth of interest in this field, with over 2,200 publications between 2014 and 2024. Top journals such as *Acta Materialia*, *Nature Communications*, and *Materials Science and Engineering A* have published the most impactful papers. Prolific authors including Wang H, Liaw PK, and Zhang Y form part of collaboration networks spanning institutions like the University of Tennessee, Oak Ridge National Laboratory, and the Chinese Academy of Sciences. The dominant geographic contributors are China, the United States, and South Korea, underscoring the global research momentum. These insights point to an increasingly interconnected research landscape, supported by cross-institutional and international collaborations that are pivotal for accelerating innovation in CCA/HEA development.

Mechanistically, the strength–ductility synergy in CCAs/HEAs arises from a confluence of effects. The stabilization of single or multi-phase

solid solutions via high configurational entropy is foundational. At the same time, heterogeneous microstructures engineered through thermomechanical processing, interstitial doping, and dual-phase design serve to initiate and propagate mechanisms such as twinning, phase transformation, and geometrically necessary dislocation accumulation. Precipitation strengthening from coherent (e.g., L12-type) and incoherent (e.g., B2-type) phases provides additional resistance to dislocation motion while maintaining deformability. These mechanisms often work synergistically, rather than additively, enabling alloys to achieve a balance of properties once thought to be mutually exclusive.

The implications of these findings are far-reaching. The development of CCAs/HEAs with robust strength–ductility combinations open new avenues for their application in sectors where structural integrity under extreme conditions is critical. In aerospace and automotive industries, these materials offer the potential for lighter, stronger components with improved energy absorption during deformation. In the energy sector, particularly for nuclear and hydrogen technologies, HEAs exhibit resistance to radiation damage and hydrogen embrittlement, positioning them as candidates for next-generation reactors and pipelines. The integration of additive manufacturing also allows for component-specific microstructural tailoring, further enhancing application potential.

Despite these advances, critical challenges remain. Scalable and reproducible processing methods, predictive modeling frameworks, and robust understanding of environmental degradation mechanisms particularly hydrogen embrittlement are still evolving. These gaps hinder broader industrial adoption and standardization. Moving forward, the field must embrace interdisciplinary approaches, integrating materials science, data-driven modeling, process engineering, and environmental sustainability. Global collaboration, open-access data initiatives, and the application of artificial intelligence to alloy design and processing optimization are essential to drive the next frontier in CCA/HEA research. As this field matures, its evolution from experimental curiosity to industrial necessity is increasingly evident, setting the stage for transformative advances in high-performance structural materials.

CRedit authorship contribution statement

Desmond Klenam: Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Olu-femi Bamisaye:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Tabiri Asumadu:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Michael Bodunrin:** Writing – review & editing, Resources, Methodology, Investigation, Conceptualization, Writing – original draft. **Winston Soboyejo:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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