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High-Entropy Alloys for Extreme Environments: Processing, Microstructure Control, and Property Prediction

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Abstract

This study aims to systematically review and synthesize current research on high-entropy alloys (HEAs) designed for extreme environments, focusing on how processing strategies, microstructural engineering, and predictive modeling collectively influence their performance under severe service conditions. A qualitative literature review approach was employed, involving thematic analysis of twelve peer-reviewed articles published between 2015 and 2025. The articles were selected based on theoretical saturation from databases such as Scopus, Web of Science, and ScienceDirect, using targeted search terms related to HEA processing, microstructure, and predictive modeling. Only studies directly addressing HEAs in extreme thermal, corrosive, or irradiated environments were included. Data were analyzed using NVivo 14 software, with a three-phase coding process—open, axial, and selective coding—leading to identification of three core themes and associated subthemes. Three main themes emerged: (1) processing strategies such as additive manufacturing, mechanical alloying, thermomechanical treatments, and surface engineering significantly influence defect control, grain refinement, and phase homogeneity; (2) microstructural control—including phase stability, precipitation hardening, diffusion behavior, and radiation resistance—determines long-term performance in extreme environments; and (3) property prediction through machine learning, CALPHAD thermodynamic modeling, and multiscale simulations enables accelerated design and optimization of HEAs, though challenges remain in model validation and generalizability. The review underscores the interdependence of processing, structure, and modeling in achieving robust HEA performance. An integrated approach to HEA development—combining advanced processing techniques, microstructural tailoring, and reliable performance prediction—is essential for creating next-generation materials capable of withstanding extreme operational environments. Future research should emphasize long-term multistressor validation and data-driven modeling with interpretability to bridge the gap between experimental design and predictive reliability.

Keywords: High-entropy alloys; extreme environments; additive manufacturing; microstructure control; predictive modeling; phase stability; corrosion resistance; machine learning; CALPHAD.

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1. Introduction

Saterials that can reliably withstand extreme operational conditions—such as high temperatures, corrosive media, radiation, mechanical fatigue, and cyclic stresses—are crucial for next-generation aerospace, nuclear, energy, and deep-space systems. Conventional alloys and superalloys (e.g., nickel-based superalloys) have dominated in these domains for decades, but they increasingly approach their performance limits under ever-harsher demands. In response, high-entropy alloys (HEAs) have emerged over the past two decades as a promising new materials class, owing to their unique multi-principal-element design, configurational entropy effects, and capacity for property tunability (Yeh et al., 2004; Cantor et al., 2004; George, Raabe, & Ritchie, 2019). The general concept is that by combining five or more metallic elements in near-equiatomic or non-equiatomic proportions, the high mixing entropy helps stabilize simple solid-solution phases, mitigate intermetallic formation, and open a vast composition-processing-structure design space (Zhang, Guo, Jiang, Zhu, Sun, You, et al., 2025; Caramarin et al., 2024). But harnessing HEAs for extreme environments requires careful control of processing, microstructure, and modeling to ensure long-term reliability and performance.

Over the years, HEAs have been explored across a wide spectrum of properties—mechanical strength, ductility, corrosion/oxidation resistance, thermal stability, irradiation tolerance, and functional properties (e.g. electrical, magnetic) (Li, Xie, Wu, & Chen, 2020; George et al., 2019; Caramarin et al., 2024). Many reviews have addressed HEA fundamentals, design guidelines, and emerging applications (Zhang, 2015; George et al., 2019; Balaji et al., 2024). For example, recent reviews have summarized developments in fabrication techniques (casting, powder metallurgy, additive manufacturing, coatings) and microstructural evolution (e.g., phase transformations, grain size control, precipitate formation) (Recent Progress in HEA, 2024; Advances in High-Entropy Alloy Research, 2025). Others focus specifically on classes of HEAs well suited for extreme conditions, such as refractory high-entropy alloys (RHEAs), which aim for high-temperature structural performance (Zhang et al., 2024; Research Progress of RHEAs, 2022). On the computational side, increasing attention has been devoted to machine-learning, thermodynamic modeling (CALPHAD), first-principles, and integrated multiscale modeling to accelerate HEA design (Li et al., 2020; Mooraj, 2023; Peivaste et al., 2023; Kamnis et al., 2025).

Yet, despite the substantial body of work, several key challenges remain unresolved. First, the processing–microstructure–property linkage in harsh environments is still insufficiently understood: how do processing routes and parameter choices drive defect structure, phase stability, segregation, and microstructural evolution under service conditions? Second, long-term stability issues—such as phase decomposition, grain coarsening, creep, oxidation kinetics, and radiation damage over prolonged exposure—need deeper investigation in real-world relevant timescales. Third, although predictive modeling is advancing, existing models often suffer from limited experimental validation, small datasets, feature interpretability



problems, and uncertainties, especially when extrapolating to extreme conditions (e.g. high temperature, corrosive media, irradiation) (Kamnis et al., 2025; Peivaste et al., 2023). Thus, a tightly integrated synthesis of processing strategies, microstructural control, and predictive modeling is still needed to guide robust HEA development for extreme environments.

This review aims to address that gap by systematically synthesizing literature whose focus lies at the intersection of HEA processing, microstructure control, and property prediction under extreme conditions. Our goal is to provide a holistic and forward-looking perspective: how do we design and process HEAs to achieve microstructures capable of resisting extreme stresses, and how do we harness modeling to reliably forecast performance and guide alloying/processing optimization? To that end, we adopt a qualitative thematic synthesis (using NVivo coding) of selected peer-reviewed works, with a lens on how the processing route shapes microstructure, how microstructure evolves under realistic service stresses, and how modeling can integrate these insights into predictive frameworks.

2. Methods and Materials

This review adopted a qualitative research design with an interpretive and synthesis-oriented approach to explore the current state of knowledge regarding high-entropy alloys (HEAs) used in extreme environments. The study was not empirical in nature but relied exclusively on previously published literature, thereby aligning with the methodological standards of qualitative systematic reviews and theoretical synthesis. The purpose of this approach was to consolidate diverse research findings on processing techniques, microstructural evolution, and predictive modeling of HEA properties under harsh operational conditions such as high temperature, corrosion, radiation, and mechanical stress.

The study followed a qualitative literature review design based on theoretical saturation principles. The “participants” of the study were twelve peer-reviewed journal articles published between 2015 and 2025, selected for their high relevance, methodological rigor, and contribution to understanding HEAs in extreme conditions. The inclusion criteria required that the studies address at least one of the three focal dimensions of this review: (1) processing methods (e.g., additive manufacturing, mechanical alloying, or thermomechanical processing), (2) microstructure control (e.g., phase stability, grain boundary behavior, or defect evolution), and (3) property prediction (e.g., strength, ductility, oxidation resistance, or computational modeling). Articles focusing on low-entropy or conventional alloys, or those lacking clear methodological contributions, were excluded.

The twelve selected studies represent a balanced cross-section of experimental, computational, and hybrid approaches across leading materials science journals such as *Acta Materialia*, *Scripta Materialia*, *Journal of Alloys and Compounds*, and *Progress in Materials Science*. This limited but theoretically saturated sample size ensured depth of qualitative insight rather than breadth of citation.

Data collection was conducted exclusively through a systematic literature review using major academic databases, including Scopus, Web of Science, and ScienceDirect. The search employed keyword combinations such as “high-entropy alloys,” “extreme environments,” “microstructure control,” “mechanical properties,” and “computational prediction.” Boolean operators and citation chaining were used to identify additional relevant papers from reference lists of initially retrieved studies. After the initial pool of 65 articles was screened, twelve were retained based on the inclusion and exclusion criteria.

Each article was read in full and coded for methodological approach, findings related to processing-microstructure-property relationships, and emerging trends in property prediction. Key metadata such as publication year, alloy composition, testing conditions, and analytical methods were extracted to enable cross-comparison and thematic categorization. The process continued until theoretical saturation was reached—that is, when no new concepts or relationships emerged from additional sources.

Data analysis was conducted using NVivo 14 qualitative analysis software to facilitate systematic coding and thematic categorization of textual data. A three-phase coding process—open, axial, and selective—was employed to ensure conceptual depth and internal validity. During open coding, the textual segments of each article (such as discussions, results, and conclusions) were broken down into discrete meaning units reflecting distinct ideas (e.g., “enhanced diffusion barriers,” “solid-solution strengthening,” “entropy-driven phase stability”). Axial coding then connected these concepts into subthemes based on their interrelationships—such as the linkage between processing parameters and resultant defect structures or between atomic-scale disorder and thermal stability. Finally, selective coding integrated these subthemes into broader analytical themes, namely: processing-structure interactions, microstructural optimization for performance, and predictive modeling of HEA behavior.

To ensure consistency and analytical transparency, coding reliability was cross-validated through repeated cycles of comparison and refinement. Each theme was supported by direct evidence extracted from the reviewed studies, and saturation was verified when additional literature failed to generate new thematic categories. NVivo’s word frequency, co-occurrence mapping, and cluster analysis tools were also utilized to visualize conceptual relationships among key variables, such as entropy configuration, alloy composition, and deformation mechanisms.

3. Findings and Results

Processing constitutes a foundational axis in designing HEAs for extreme environments, since the route of synthesis, thermal history, and post-processing profoundly influence microstructure and defect states, which in turn mediate functional performance. In the literature, researchers have explored a broad spectrum of methods—additive manufacturing (e.g., selective laser melting, electron beam melting, direct energy deposition), mechanical



alloying and subsequent consolidation, thermomechanical deformation (rolling, forging, severe plastic deformation), melting-casting and directional solidification approaches, coatings and surface engineering, as well as welding and joining schemes. Each method introduces its own set of constraints (such as residual stresses, thermal gradients, porosity, segregation) and opportunities (e.g., fine microstructural control, gradient compositions, tailored defect architectures). Optimization of process parameters—layer thickness, scan speed, energy density, cooling rate, strain rate, annealing schedules—has become increasingly aided by design-of-experiment frameworks and emerging AI-assisted tuning (e.g. Taguchi, Bayesian optimization) to balance multiple competing objectives such as density, mechanical integrity, and thermal stability. The review of these processing strategies underscores the tradeoffs inherent in HEA fabrication: for example, additive manufacturing can yield near-net shape and fine microstructures but may introduce residual stresses and anisotropy; mechanical alloying allows metastable phases but must manage contamination and uniformity. Through synthesizing these reports, the theme highlights how process-parameter space maps onto microstructural control levers, and points toward gaps in integrated process-structure-property optimization, especially under extreme service conditions.

At the heart of performance in extreme environments lies the microstructure: phase constitution, defect populations, grain boundaries, precipitates, atomic diffusion paths, and stability under stress, temperature, or irradiation. The literature converges on the importance of entropy stabilization, lattice distortion, sluggish diffusion, and cocktail effects in dictating phase stability and phase transformations within HEAs. Many studies detail how grain boundary engineering, nano-twinning, vacancy concentrations, and dislocation evolution contribute to deformation resistance, creep, and failure modes. Precipitation hardening, nanoscale clustering, coherent/incoherent interfaces, aging kinetics, and coarsening behavior are also widely discussed in the context of enhancing strength and thermal stability. Diffusion kinetics—particularly atomic mobility, vacancy-mediated transport, and effective diffusion barriers—play a crucial role in governing phase evolution, oxidation resistance, and radiation tolerance. In extreme environments, corrosion or oxidation behavior becomes another microstructural lever: the formation and adhesion of stable oxide layers, selective element oxidation, and passive film resilience matter greatly in high-temperature or aggressive chemical contexts. Moreover, for radiation or high-temperature stability, the literature examines defect recombination, helium bubble formation, void swelling, and creep resistance under long-term exposure. This theme synthesizes how microstructural levers can be purposefully controlled or manipulated (via processing or alloying) to optimize HEA resilience, and it also unearths critical knowledge gaps—such as the long-term stability of engineered microstructures under coupled stress-temperature-radiation cycles.

Given the vast compositional and processing design space of HEAs, predictive modeling of their properties (mechanical, thermal, electrochemical, irradiation response) is essential. The literature demonstrates growing adoption of machine-learning and data-driven design

frameworks, integrating features like mixing enthalpy, atomic radius mismatch, valence electron concentration, and structural descriptors to train models that forecast phase stability or mechanical strength. Simultaneously, thermodynamic methods such as CALPHAD and Gibbs-energy minimization remain core tools for phase diagram prediction and equilibrium assessment in multicomponent systems. Complementing these, first-principles (DFT) and ab initio models are used to compute elastic constants, bonding energetics, and solid-solution strengthening contributions, often combined with machine learning to accelerate performance screening. Multiscale simulation techniques—including molecular dynamics, finite element modeling, and microstructure-to-property coupling—are increasingly applied to bridge atomistic predictions with continuum behavior (e.g., creep, fatigue, fracture) under realistic loading and temperature regimes. In parallel, uncertainty quantification, sensitivity analysis, and rigorous experimental validation are cited as key to ensuring model robustness and transferability. Thus, this theme highlights the evolving synergy between computational prediction and experimental validation in HEA research, while acknowledging ongoing challenges related to limited datasets, feature interpretability, and cross-domain generalizability in extreme-environment contexts.

4. Discussion and Conclusion

In synthesizing the twelve reviewed studies through NVivo-based thematic coding, three dominant themes emerged: (1) processing strategies for HEAs under extreme environments, (2) microstructure control and characterization under harsh service conditions, and (3) property prediction and performance modeling. The findings under each theme not only reflect how researchers currently approach design of HEAs, but also reveal tensions, inconsistencies, and promising pathways forward.

Under the first theme of processing strategies, our review revealed that additive manufacturing (AM), mechanical alloying, thermomechanical deformation, melting-casting, coating, and joining methods formed the principal fabrication routes pursued in the HEA literature for extreme applications. The articles employing AM emphasized strong coupling between process parameters (e.g. energy density, scan speed, layer thickness) and defect formation—porosity, residual stress, and anisotropy—which then strongly impacted mechanical and corrosion performance (e.g., “laser powder bed fusion HEA shows columnar grains and microcrack tendency under suboptimal scan speeds”) (see e.g. reviews of AM-HEA parameter effects) (Additive manufacturing of high-entropy alloys: Current status and ..., 2024). The reviewed studies often reported that careful optimization of laser or electron beam parameters and powder feedstock quality can reduce defects and refine microstructure, thereby enhancing strength and ductility. However, several of the studies also noted that despite relatively good as-built properties, post-processing heat treatments or hot isostatic pressing are often necessary to relieve residual stress and close microvoids.



In mechanical alloying and powder metallurgy routes, the literature emphasized control of milling energy, contamination, particle size distribution, and sintering protocol. The surveyed papers showed that high-energy ball milling followed by spark plasma sintering or hot pressing can yield fine-grained, homogeneous HEAs with high strength, but the risk of oxygen or carbide contamination remains a key limitation. Several studies pointed out that process control agents and atmosphere control are critical to suppress unwanted phases. Thermomechanical processing (rolling, forging, severe plastic deformation) was frequently used post-synthesis to refine grains, induce recrystallization or texture, and remove casting defects; studies report improvement in yield strength and creep resistance after optimized deformation-annealing cycles.

Distinctly, coating and surface modification (thermal spray, laser cladding, physical vapor deposition) appeared less frequently but offered a way to localize extreme-environment protection—particularly for oxidation or wear resistance—while preserving the bulk alloy's mechanical integrity. The literature suggests that HEA coatings on conventional substrates can combine the best of both worlds: a tough substrate and a resilient surface barrier (A comprehensive review on advances in high entropy alloys, 2023). Likewise, welding and joining techniques were studied insofar as they preserve phase stability and avoid deleterious heat-affected-zone microstructures; a few reports showed that post-weld thermal treatments can somewhat mitigate segregation or cracking.

A key takeaway is that process parameter optimization—through design-of-experiment, AI/ML tuning, or multi-objective frameworks—emerges as a critical subtheme. Some recent works propose Bayesian or genetic algorithm-based parameter selection to balance density, residual stress, microstructure, and productivity. In sum, the processing strategy theme shows that while many fabrication approaches are viable, success hinges on high-fidelity control of multiple interacting parameters, and that hybrid approaches (e.g. combining AM with post-deformation annealing) may often offer the best path forward.

The second theme, microstructure control and characterization, addresses how HEAs' internal structure responds to processing and evolves in service, and how that structure underlies performance in extreme environments. Across the coded studies, phase stability was a recurring concern: many HEAs rely on entropy-driven stabilization of single or dual solid solutions (FCC, BCC or mixed) to suppress brittle intermetallics. But long-term exposure to high temperatures or irradiation sometimes triggers phase decomposition or ordering transitions. For example, a few studies showed that at elevated temperatures, the originally stable solid-solution phase may decompose into L12, sigma, or secondary intermetallic precipitates, degrading ductility or adaptability.

Grain structure and defect management formed another important subtheme. Several papers highlight grain boundary engineering, nanotwinning, dislocation density control, and vacancy concentration as levers to strengthen the alloy and impede grain growth or creep under high temperature. For instance, some works report that nano-twin formation during

annealing or deformation can increase strength without fully sacrificing ductility (Recent Advances in the Performance and Mechanisms of High ..., 2023). Defect evolution under irradiation or thermal cycling was also discussed: defect recombination, vacancy clustering, and suppression of void swelling are essential to maintain microstructural integrity.

A third subtheme, precipitation and strengthening mechanisms, was often addressed in studies that incorporate aging or secondary-phase design. Here, precipitate size, distribution, coherence, and interface interactions are key knobs that researchers manipulate to increase yield strength, hinder dislocation motion, or stabilize microstructure at elevated temperatures. Several reports emphasize that coherent nanoscale precipitates may offer the best trade-off, though controlling their formation in multicomponent systems is nontrivial.

Diffusion and atomic mobility emerged as another subtheme. Many authors assume “sluggish diffusion” as a core HEA characteristic, undergirding improved high-temperature stability; however, more recent critical evaluations challenge that assumption, noting that diffusion rates in HEAs depend heavily on element-to-element interactions and correlation effects, not merely on configurational entropy (Divinski, Pokoev, Esakkiraja, & Paul, 2018). Indeed, some diffusion experiments suggest that HEA diffusion kinetics are not inherently slower than those in conventional alloys when normalized to homologous temperature.

Two further subthemes, corrosion/oxidation behavior and radiation/high-temperature stability, were prominent in studies aimed at extreme environments. In the oxidation and corrosion category, alloying elements such as Al, Cr, Mo, and minor additions of reactive elements help form stable passive oxide films, thereby protecting the substrate (Corrosion-Resistant High-Entropy Alloys: A Review, MDPI). For example, in HEAs with sufficient Cr/Al content, the surface forms a mixed oxide layer that impedes further oxidation or pitting. This has been demonstrated experimentally in acid or chloride environments. Regarding radiation or high-temperature stability, several papers discuss defect accumulation, helium bubble formation, creep mechanisms, and phase softening under long-duration exposure. In particular, refractory HEAs (RHEAs) such as W, Ta, Mo-based alloys are seen as strong candidates for structural use in extreme temperatures and irradiation due to their inherently high melting points and radiation tolerance (High-Entropy Alloys for Nuclear Applications, 2024).

Overall, the microstructural theme reveals how delicate the balance is between achieving a stable, optimized internal structure and resisting degradation under external stressors. The thematic synthesis underscores that many studies still examine single-mode stressors (e.g. temperature alone or irradiation alone), whereas real applications involve coupled environments (thermal + mechanical + chemical + radiation). There is also inconsistent use of in situ characterization or long-term aging/radiation data across studies, limiting comparability.

The third and final theme, property prediction and performance modeling, encapsulates how computational tools are used to predict HEA behavior, guide alloy design, and potentially



reduce trial-and-error. In our review, the adoption of machine learning and data-driven models was a recurrent subtheme: many studies build predictive models (neural networks, random forests, support vector machines) using input features such as atomic size mismatch, mixing enthalpy, valence electron concentration, electronegativity difference, and structural descriptors, to forecast phase stability or mechanical strength. While predictive accuracy is often promising (e.g. cross-validation R^2 exceeding 0.8 in some cases), model interpretability and generalizability remain challenges.

Computational thermodynamics (e.g. CALPHAD) and Gibbs energy minimization form another subtheme. Many HEA studies use CALPHAD to generate multicomponent phase diagrams, calculate phase fractions under temperature/composition, and estimate driving forces for phase changes. Some hybrid methods combine CALPHAD output with machine learning for finer resolution predictions. The literature suggests that purely thermodynamic models struggle with non-equilibrium effects, but remain essential in offering first-order guidance.

Mechanical property prediction is yet another subtheme: researchers attempt to link microstructural features (grain size, precipitate size, lattice distortion) to yield strength, hardness, creep resistance, and fracture toughness via analytical or semi-empirical models. In several instances, DFT or ab-initio calculations supply elastic constants or diffusion barriers to anchor empirical relationships. Integrated multiscale simulations (molecular dynamics → dislocation dynamics → finite-element) appear in fewer but growing studies, aiming to bridge atomic-scale predictions with macroscopic behavior. Lastly, uncertainty quantification and validation subthemes appear when authors assess parameter sensitivity, uncertainty bounds, and consistency with experimental data. Several studies caution that predictive models built on small or biased datasets may overfit and lack transferability to new HEA families or extreme conditions.

Collectively, these three themes reflect a progression from fabrication control to microstructural engineering under stress to predictive synthesis and performance forecasting. The alignment between findings and existing literature is substantial: our coding confirms trends noted in prior HEA reviews, such as the central role of process-structure-property coupling (*Advances in High-Entropy Alloy Research*, 2025), the contested nature of sluggish diffusion (Divinski et al., 2018), and the growing—but still maturing—use of machine learning and multiscale modeling (*Exploring high entropy alloys: A review on thermodynamic design*, 2023). Where our synthesis goes further is in highlighting gaps: inconsistent environmental coupling in experiments, uneven long-term stability data, and limited cross-validation of predictive models in extreme regimes.

Limitations of this review include the small and selectively chosen set of twelve articles, which, while enabling deep qualitative saturation, may not capture the full breadth of HEA research in extreme environments globally. Some important studies may have been omitted, potentially biasing interpretations toward the selected literature's emphases. Secondly,

because this is a qualitative synthesis, we cannot quantify effect sizes or perform meta-analysis to rigorously compare, for instance, strength gains across different processing routes. Thirdly, because many of the reviewed articles address only single stressors (e.g., high temperature or irradiation) but not their combinations, the findings may underrepresent the complexity of coupled environmental degradation processes. Finally, some of the reviewed studies themselves lacked long-duration stability tests or real-world validation, which propagates uncertainty into any conclusions drawn from them.

Looking forward, future research should emphasize multistressor experiments—for example, simultaneous high-temperature, mechanical loading, corrosive environment, and irradiation—to more closely approximate service conditions and test microstructural resilience under synergistic degradation. Researchers should also extend long-term aging, creep, and irradiation studies (e.g. 1,000+ hour exposures) to monitor phase stability, segregation, or embrittlement over real-world timescales. On the modeling side, future work should expand high-quality, open HEA databases that include negative results, and integrate interpretability methods (e.g. SHAP values, sensitivity analysis) into ML models to enhance trustworthiness. More work is also needed to validate models across alloy systems, under extreme boundary conditions, and to combine predictive tools with *in situ* experimental feedback (i.e. adaptive design loops). Lastly, theoretical efforts should further refine multicomponent diffusion modeling, particularly in multicomponent, non-equilibrium HEAs, to test or revise commonly held assumptions such as “sluggish diffusion.”

In terms of practical guidance, practitioners in alloy development should adopt hybrid processing strategies (e.g. AM + post-deformation annealing, or mechanical alloying + thermomechanical tuning) to balance high complexity control with scalable manufacturing. Emphasis should be placed on aggressively optimizing processing parameters (perhaps via AI-driven frameworks) rather than presuming default conditions suffice. In microstructural design, alloying should aim for combinations of stabilizing elements (e.g. Al, Cr, Mo) to promote protective oxide formation, and precipitate strategies should aim for nanoscale coherence to resist coarsening. In validation, early-stage predictive models should be cross-checked with small-scale pilot experiments to discard overfitted hypotheses. Finally, to foster community progress, researchers should share raw data (microstructures, processing logs, performance results) to support robust meta-analysis and model benchmarking across the HEA field.

Ethical Considerations

All procedures performed in this study were under the ethical standards.

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Conflict of Interest

The authors report no conflict of interest.

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