

High Entropy Ceramics: A Brief Introduction

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Abstract

This paper provides a concise introduction to high entropy ceramics (HECs) within the context of materials science. It emphasizes the pivotal role of entropy in influencing HEC behavior and elucidates their distinctive properties. The article also undertakes a comprehensive review of the latest developments in HEC research and their potential utilization in challenging environments, offering a glimpse into the forthcoming discussion.

Keywords: materials, entropy, high entropy ceramics

1. Introduction

Ever since their discovery in 2004, significant research efforts have been dedicated to processing and characterizing metallic High Entropy Alloys (HEAs). These alloys are known for their superior physical and mechanical properties, such as high strength, outstanding wear resistance, and excellent high-temperature strength [1-3]. The concept of high entropy has been extended to ceramics (HECs), polymers, and composites, which mirror the structural characteristics of HEAs. HECs consist of a diverse range of materials, including oxides, borides, carbides, nitrides, silicides, carbonitrides, and the newly developed dual-phase HECs [4-6]. This article provides a brief introduction to the development, properties, and potential applications of HECs, with a specific emphasis on ultra-high-temperature variants. Figure 1 provides an overview of various types of high-entropy materials, with a special focus on HECs.

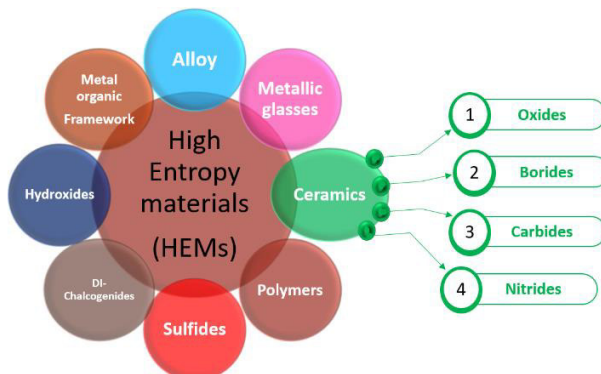


Figure 1. Various types of high entropy materials, with a focus on HECs

2. Definition of HECs and their precursors

The stability of a solid solution, determined by Gibbs free energy changes (ΔG_{mix}), relies on factors such as mixing entropy (ΔS_{mix}), enthalpy (ΔH_{mix}), and absolute temperature (T).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

Elevating mixing entropy reduces Gibbs free energy, enhancing the stability of solid solutions. Entropy, influenced by temperature, element count, and atomic fraction, crucially determines the thermodynamic stability, especially in equiatomic mixtures. In equiatomic mixtures, the mixing entropy can be determined by [5]:

$$\Delta S_{mix} = R \ln N \quad (2)$$

The correlation between mixing entropy and the number of elements N in equiatomic mixtures, as depicted in Figure 2, suggests a practical strategy to augment entropy, enhancing the stability of single-phase materials [5]. This process not only ensures high phase stability but also yields excellent properties, attributed to elements' co-contributions through phenomena like the cocktail effect, valence electron distribution, lattice distortion, and sluggish diffusion. There are two key definitions for high-entropy ceramics: one underscores equiatomic or near equiatomic ratios of five or more principal elements (5–35% atomic percentage) for solid solution phase formation, and the other centers on a configurational entropy surpassing 1.61 (or 1.5 in some references) times the gas constant "R" in their random solution state.

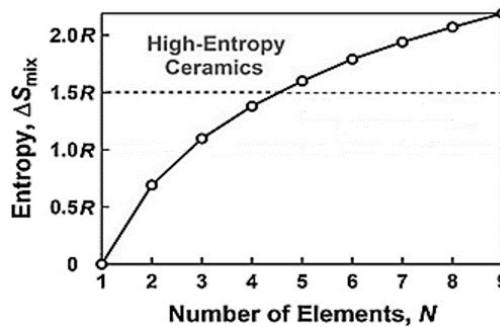


Figure 2. Relation between entropy and number of elements defining high entropy ceramics [5]

Considering recent publications, it is essential to address certain issues related to the terminology, especially concerning dual-phase development in high-entropy ceramics (HECs). A proposed solution introduces the concept of compositionally-complex ceramics or multi-principal cation ceramics, aiming to comprehensively encompass these materials [4-6].

3. Advancements in high entropy ceramics

3.1 Development approaches

Various methods have been explored by researchers for creating high-entropy ceramics. Each method presents its unique advantages and challenges. Two primary approaches exist for this

purpose: experimental and computational. The experimental approach involves processing, microstructure analysis, and functional/mechanical property testing. On the other hand, the computational approach involves calculating Gibbs free energy using various methods such as density functional theory, molecular dynamics simulation, machine learning, CALPHAD, and descriptors. This approach also involves describing high-entropy systems using entropy-forming ability calculations, lattice size difference calculations, and valence electron concentration.

Recent research has demonstrated that the hardness of transition metal rock salt carbides and carbonitrides is correlated with their valence electron concentration (VEC), which is also true for HECs. In the field of experimental materials processing, solid-state reaction methods are widely employed for materials preparation. These methods include ball milling, high-pressure torsion, spark plasma sintering/hot pressing, reactive spark plasma sintering, and self-propagating high-temperature synthesis. Various methods, such as X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, are employed to examine the microstructure characteristics of the prepared ceramics. It is crucial to conduct chemical analyses of the developed systems to determine the distribution of individual elements. The most commonly studied properties are density, elastic modulus, and hardness, although there are also studies that investigate strength, fracture toughness, creep, and oxidation resistance [6]. Figure 3 illustrates the development cycle schema for high entropy ceramics [4,18].

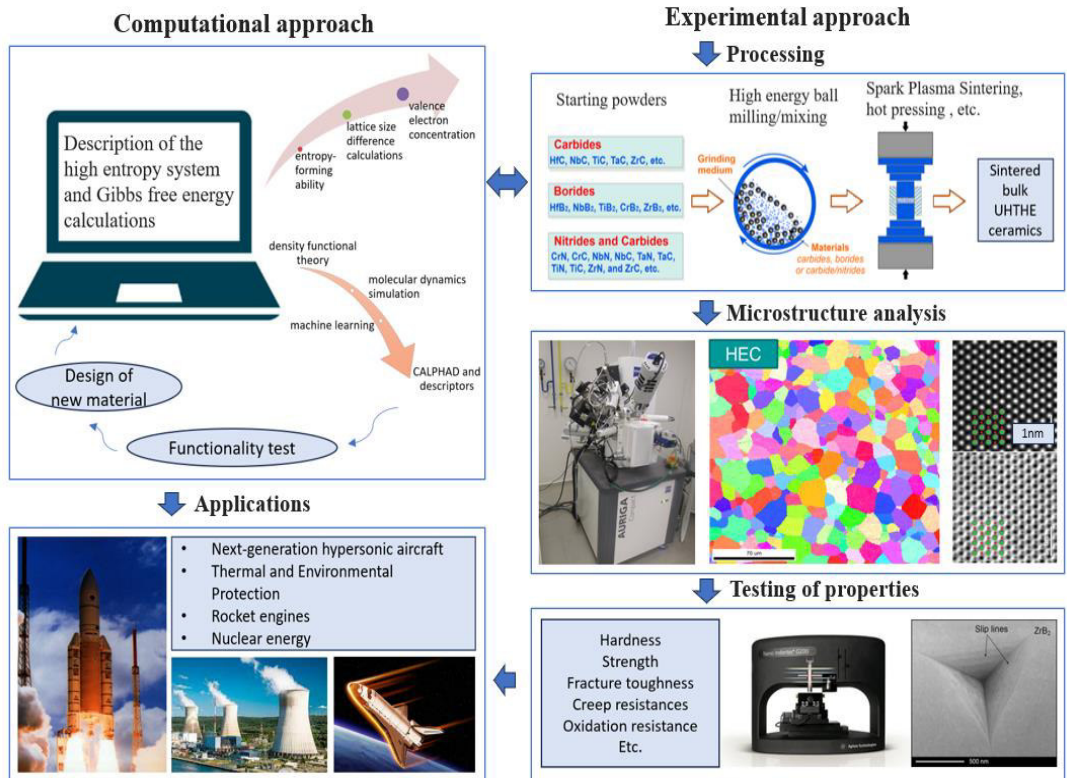


Figure 3. Development cycle schema for high entropy ceramics [4, 18].

3.2 Evolution timeline of bulk HECs

Bulk High Entropy Ceramics (HECs) were first reported in 2015 in the form of oxide [10]. Since then, the number of reports dealing with HECs has rapidly increased, indicating the timeliness and global technological importance of this research field. New HEC systems comprise various chemical compositions such as rock salt, perovskite, fluorite, oxides, borides, carbides, silicides, nitrides, and more. In 2016, Gild et al. [11] successfully synthesized six single-phase, high-entropy, metal diborides using mechanical alloying and SPS. The densities were greater than 92%, and the compositions were mostly uniform at the nanoscale and microscale. Initial property assessments showed that both the hardness and oxidation resistance of these high-entropy metal diborides were generally better than the average performance of individual metal diborides made using the same processing route. In 2018, E. Castle et al. [12] processed and characterized (Hf-Ta-Zr-Ti)C & (Hf-Ta-Zr-Nb)C high entropy UHTC carbide composites via ball milling and Spark Plasma Sintering (SPS). They reported that the lattice parameter mismatch of the component monocarbides is a key predictive factor for determining solid solution formation. Thus, a four-metal (Hf-Ta-Zr-Nb)C composition formed a single-phase solid solution more readily than the (Hf-Ta-Zr-Ti)C composition. In 2020, Dippo et al. [13] reported the first synthesis of bulk high-entropy nitrides and carbon-nitrides and investigated the effect of configurational entropy and valence electron concentration on the mechanical properties of bulk high-entropy ceramics. Also in 2020, M. Qin et al. [14] reported the development of dual-phase high-entropy UHTCs (DPHE-UHTC's). The high-entropy boride and carbide solid-solution phases formed in equilibria with each other, where a thermodynamic relation exists to govern the non-equal partition of each metal element. According to their results, this new class of HECs provides a new platform to tune characteristics/properties, including grain size, hardness, modulus, and thermal conductivity in addition to other mechanical and fracture properties, similar to metallic dual-phase HEA's. Recently, Luo et al. [15] synthesized single-phase high-entropy boride and carbide ceramic powders, together with dual-phase high-entropy powders via a simple one-step boro/carbothermal reduction approach at 1650°C, which were then sintered via SPS processing at 2000°C. A new reactive sintering route was recently applied by Huo et al. [16] to process dual-phase high-entropy ceramics using ZrB₂, NbB₂, HfB₂, TaB₂, and TiC as starting materials. Very high relative density was reached during sintering at 2000°C for 1 hour, with excellent mechanical properties such as hardness 28.4 ± 1.5 GPa, bending strength 1017 ± 91 MPa, and fracture toughness 4.7 ± 0.3 MPa·m^{1/2} with 50 mol% TiC addition..

4. Unique properties for unique applications

4.1 Mechanical properties

High-entropy ceramics exhibit improved mechanical properties through a combination of grain refinement and solid-solution strengthening. Lattice distortions, attributed to varying atomic radii and Jahn-Teller effects, create barriers that impede dislocation propagation, increasing hardness and yield strength while limiting plastic deformation. Additionally, reduced grain coarsening is linked to heightened crystalline energy due to lattice distortions, slowing diffusion and resulting in finer grains. This finer grain structure enhances toughness by facilitating crack deflection at grain boundaries and enabling Hall-Petch strengthening, which restricts dislocation motion [16]. They demonstrate high nano hardness values, even under substantial loads. This indicates their potential for robust mechanical performance, making them suitable for demanding applications [17]. Moreover, nanotechnology emerges as a key player, holding the potential to optimize the toughness of high-entropy ceramics, with nanoscale additives offering precise control over material characteristics. It opens the door to the development of more fracture-resistant and damage-tolerant

ceramics. Figure 4 shows the characteristic values of hardness and fracture toughness in the case of advanced HECs [19-21].

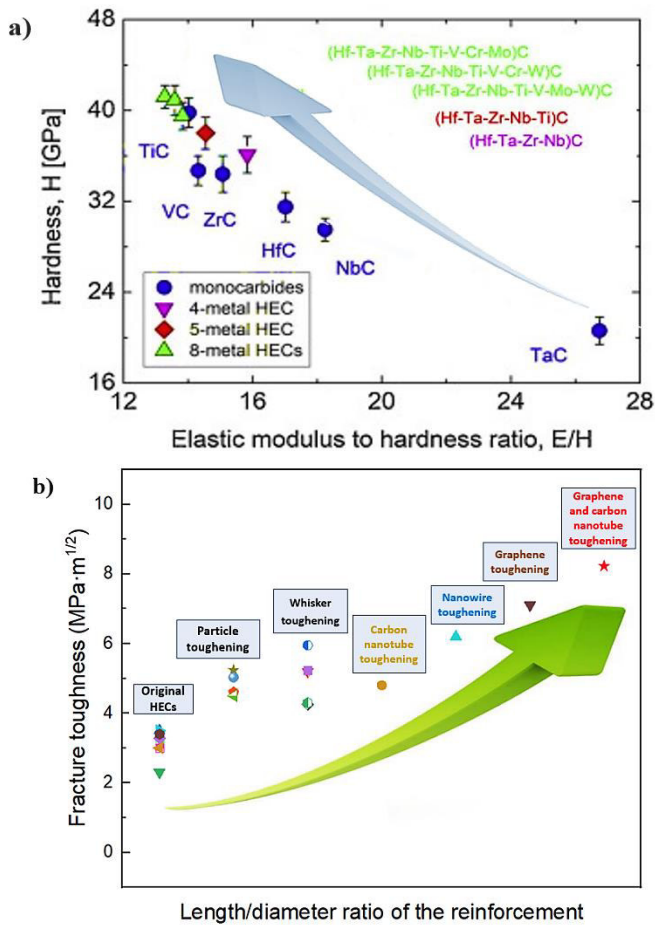


Figure 4. a) Elastic modulus to hardness ratio as a function of hardness, and b) property enhancement via various nano reinforcements [19-21]

4.2 Thermal resistance

In high-entropy ceramics (HECs), disorder plays a crucial role in reducing lattice thermal conductivity while maintaining the material's mechanical strength and stiffness. These ceramics, characterized by high melting temperatures in carbides and borides, hold significant promise for applications in demanding environments, including combustion chambers and other extreme conditions. The advantageous thermal properties of HECs, such as low thermal conductivity, stem from the phonon scattering effect resulting from their multi-component composition and distorted lattice structure. The interplay between elastic modulus and thermal conductivity is pivotal for comprehending these thermal characteristics and is frequently explored alongside their mechanical properties in academic research [5,16].

4.3 Corrosion and wear resistance

Carbides and borides have high melting temperatures, making them ideal for use in extreme environments like combustion chambers. High-entropy ceramics with passivating oxide layers can withstand high temperatures under oxidizing conditions. High-entropy carbides and borides combine many elements to tailor chemical properties, making them strong candidates for use in extreme heat conditions. A recent study showed that (Hf-Zr-Ta-Nb-Ti)C system has high hardness of 38.5 ± 0.5 GPa and 35.5 ± 1.0 GPa for high-entropy carbide grains and grain boundaries, respectively [20]. The wear mechanism in this system was mainly due to mechanical wear with limited grain pull out and localized trilayer formation, Figure 5.

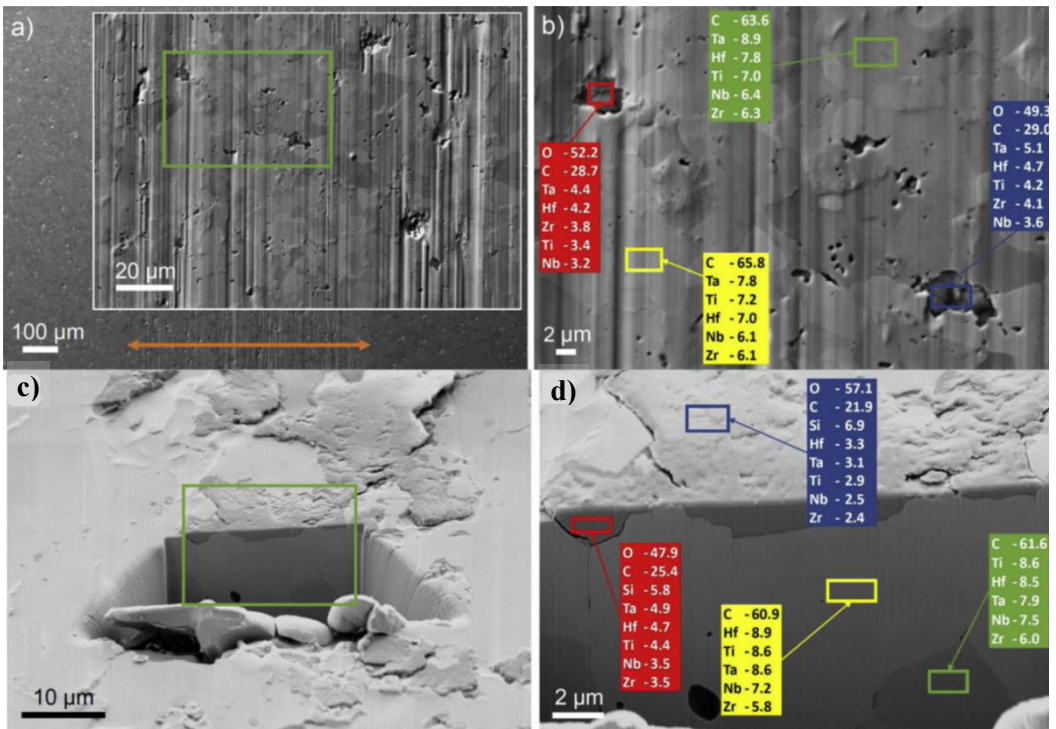


Figure 5. Wear characteristics of the (Hf-Zr-Ta-Nb-Ti)C system with chemical composition of the wear tracks, [20]

5. Summary and future outlook

Based on current published results, the exploration of high entropy ceramics reveals a vast compositional frontier, offering potential for novel materials with enhanced properties and significant implications for future applications. The adaptability in crystal structures, achieved through diverse atom selection, facilitates the tailoring of properties by adjusting composition and structure. Computational methods play a crucial role in predicting thermal expansion, thermal conductivity, and electrical conductivity, elucidating atomistic and electronic structure effects. Precise atomic-level characterization is essential for understanding element distribution and local bonding in these complex systems. To meet the demands for improved fracture toughness, bending strength, and high-temperature properties, concerted efforts are required, including advancements

in powder synthesis and densification methods. These developments aim not only to produce higher quantities of powders but also to create larger ceramic parts without compromising on impurity content or microstructural uniformity, laying the groundwork for future industrial-scale production and commercialization of these groundbreaking materials.

6. References

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