

# ***High Entropy & Compositionally Complex Ceramics (HECs/CCCs): A Review on Design, Processing, Properties and Emerging Applications***

***Dinesh Kumar Verma<sup>1</sup>, Ayesha N. Qureshi<sup>2</sup>, Mahesh B. Kale<sup>3</sup>***

*Department of Civil Engineering*

*Government College of Engineering, Kalahandi*

***Email: Dineshkverma2y@gmail.com<sup>1</sup>, qureshiayasha4n@rediffmail.com<sup>2</sup>, maheshbkalesk@yahoo.com<sup>3</sup>***

## ***ABSTRACT***

*High Entropy Ceramics (HECs) and Compositionally Complex Ceramics (CCCs) are new class of advanced ceramic materials derived from the concept of high entropy alloys. Instead of one or two principal elements, these ceramics consist of multiple principal cations in near equal proportion forming single phase solid solutions. Such unusual composition leads to exceptional thermal stability, mechanical strength, and oxidation resistance and radiation tolerance. In recent years, researchers are showing interest towards HECs because of their promising applications in extreme environments such as aerospace, nuclear reactors, cutting tools and thermal barrier coatings. This review paper discusses the fundamental concept, thermodynamic principles, synthesis methods, microstructural characteristics, mechanical and functional properties and recent applications of HECs/CCCs. Also challenges in fabrication and future research direction are highlighted. Although this field is still developing, HECs are expected to play an important role in next generation structural and functional ceramics.*

***KEYWORDS: High Entropy Ceramics, Compositionally Complex Ceramics, Solid Solution, Thermal Stability, Ultra-High Temperature Ceramics, Advanced Materials***

## INTRODUCTION

Traditional ceramics are generally composed of one major component such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$  etc. Their properties mainly depend on purity and microstructure. However, the concept of entropy stabilized materials has changed the way materials are designed. Inspired from High Entropy Alloys (HEAs), scientists extended the idea to ceramic systems and developed High Entropy Ceramics.

HECs contain five or more cations mixed in equiatomic or near equiatomic ratio which form a single phase crystal structure. Instead of multiphase mixture, the configurational entropy stabilizes the structure. These materials also called as Compositionally Complex Ceramics (CCCs).

The interest in HECs comes from their superior hardness, oxidation resistance, thermal shock resistance and chemical inertness. In many cases, they show better performance than conventional ceramics.

## CONCEPT OF HIGH ENTROPY IN CERAMICS

High Entropy Ceramics (HECs) are based on the idea of **maximizing configurational entropy** to stabilize complex compositions. Traditionally, ceramics contain one or two primary cations, and adding more elements often leads to multiple phases or intermetallic compounds. In HECs, however, the combination of **five or more cations in near-equiatomic ratios** creates a **highly disordered yet single-phase system**, which is thermodynamically stabilized by entropy.

### 1. Thermodynamic Basis

The Gibbs free energy (GGG) of a system determines phase stability:

$$G = H - T \Delta S$$

Where:

- $H$  = Enthalpy of formation
- $T$  = Absolute temperature
- $\Delta S$  = Entropy

In HECs, the **configurational entropy ( $\Delta S_{\text{config}}$ )** is significantly high due to the presence of multiple cations:

$$\Delta S_{\text{config}} = -R \sum_{i=1}^n c_i \ln c_i \quad \Delta S_{\text{config}} = -R \sum_{i=1}^n c_i \ln c_i$$

For **equimolar compositions**,  $c_i = 1/n$ , which simplifies to:

$$\Delta S_{\text{config}} = R \ln n \quad \Delta S_{\text{config}} = R \ln n$$

Where:

- $R$  = Gas constant (8.314 J/mol·K)
- $n$  = Number of distinct cations

**Implication:** As  $n$  increases, the entropy term ( $T \Delta S$ ) becomes more negative, lowering Gibbs free energy and **favoring the formation of a single-phase solid solution** instead of multiple competing phases. This is the fundamental principle behind entropy stabilization.

**Example:**

A ceramic composed of 5 cations like (Hf, Zr, Ti, Nb, Ta)C achieves  $\Delta S_{\text{config}} = R \ln 5 \approx 1.61R$ , which is sufficient to stabilize a single-phase rock-salt carbide structure at high temperature.

**2. Core Effects in HECs**

The exceptional properties of HECs arise from four interconnected effects:

**A. High Entropy Effect**

- The high configurational entropy **stabilizes single-phase solid solutions**, even when traditional phase diagrams predict multiple phases.
- This effect allows cations with different chemical properties to coexist without phase separation.
- **Example:** (Mg, Co, Ni, Cu, Zn)O forms a single rock-salt structure, although individually these oxides might not form such a solid solution.

**B. Lattice Distortion**

- Mixing cations with **different ionic radii** introduces **local lattice strain**, distorting the crystal lattice.

- Lattice distortion strengthens the material via **solid solution strengthening**, as dislocations have difficulty moving.

**Example:** In (Hf, Zr, Ti, Nb, Ta)C, the lattice constants vary slightly among cations, creating internal stresses that enhance hardness and fracture resistance.

### C. Sluggish Diffusion

- The complex lattice structure **reduces atomic mobility**.
- Sluggish diffusion slows down grain growth and phase transformations at high temperatures.
- This improves **thermal stability**, creep resistance, and oxidation resistance, making HECs suitable for extreme environments.

**Example:** Carbide HECs maintain fine microstructures even after prolonged exposure to 2000°C.

### D. Cocktail Effect

- HECs show **synergistic enhancement of properties**, often exceeding the simple average of the constituent ceramics.
- The combination of multiple elements leads to **unique mechanical, thermal, and chemical behavior** that cannot be achieved in traditional single-component ceramics.

**Example:** A HEC may simultaneously exhibit high hardness, oxidation resistance, and radiation tolerance due to the interplay of its multiple cations.

### Summary of Stabilization Mechanism

1. High configurational entropy reduces Gibbs free energy.
2. Lattice distortion enhances mechanical properties.
3. Sluggish diffusion improves thermal stability.
4. Cocktail effect provides multifunctional performance.

### TYPES OF HIGH ENTROPY CERAMICS (HECS)

High Entropy Ceramics (HECs) can be categorized based on their **anion chemistry** and **crystal**

**structures.** By incorporating five or more cations in near-equimolar ratios, these ceramics form **single-phase solid solutions**, exhibiting enhanced mechanical, thermal, and chemical properties. Depending on the anion type, HECs are classified as **oxides, carbides, nitrides, borides, silicides, or hybrid systems.**

### 1. High Entropy Oxides (HEOs)

- **Composition:** Multiple metal cations combined with oxygen, typically in a **rock-salt, fluorite, or spinel structure.**

#### Examples:

- (Mg, Co, Ni, Cu, Zn)O – rock-salt structure
- (Co, Cr, Fe, Mn, Ni)<sub>3</sub>O<sub>4</sub> – spinel structure
- (Ce, Zr, Hf, Ti, La)O<sub>2</sub> – fluorite structure

#### Properties:

- High thermal stability
- Resistance to oxidation and corrosion
- Tunable electrical and magnetic properties
- **Applications:** Catalysts, solid oxide fuel cells, thermal barrier coatings.

#### Mechanism:

High configurational entropy stabilizes single-phase solid solutions even when constituent oxides usually form separate phases.

### 2. High Entropy Carbides (HECs/HECCs)

- **Composition:** Multiple transition metal carbides (e.g., TiC, HfC, TaC, ZrC, NbC) forming a **face-centered cubic (FCC) structure.**

**Examples:** (Hf, Ta, Zr, Nb, Ti)C

#### Properties:

- Ultra-high hardness (30–40 GPa)
- Excellent wear resistance
- High melting point (>3500°C)

- Oxidation resistance improved at high temperature

**Applications:** Cutting tools, ultra-high temperature components in aerospace and nuclear applications.

**Mechanism:**

Sluggish diffusion and lattice distortion enhance high-temperature mechanical strength and creep resistance.

**3. High Entropy Nitrides (HENs)**

- **Composition:** Transition metal nitrides forming FCC or hexagonal lattices.
- **Examples:** (Ti, Zr, Hf, Nb, Ta)N, (Cr, Mo, W, V, Ti)N

**Properties:**

- High hardness and elastic modulus
- Excellent oxidation and corrosion resistance
- High melting temperature

**Applications:** Protective coatings, hard coatings, high-temperature electronics.

**Mechanism:**

Nitrogen atoms occupy interstitial sites, while multiple cations in the metal sublattice stabilize the structure and improve thermal and chemical stability.

**4. High Entropy Borides (HEBs)**

- **Composition:** Transition metal borides with hexagonal close-packed (HCP) structures.  
**Examples:** (Hf, Zr, Ti, Ta, Nb)B<sub>2</sub>, (Mo, W, Ti, Zr, Hf)B<sub>2</sub>

**Properties:**

- Ultra-high hardness
- Thermal stability up to 3000°C
- Oxidation resistance enhanced by complex boride surface layer

**Applications:** Aerospace, high-temperature structural components, cutting tools.

**Mechanism:**

Multiple cations create lattice distortion, improving fracture toughness and high-temperature stability compared to traditional borides.

**5. High Entropy Silicides (HESs)**

- **Composition:** Multi-principal element silicides forming tetragonal or hexagonal crystal structures.

**Examples:** (Mo, Nb, Ta, Ti, W)Si<sub>2</sub>

**Properties:**

- High-temperature strength
- Oxidation and thermal shock resistance
- Moderate electrical conductivity

**Applications:** High-temperature structural components, thermoelectrics, electronic devices.

**Mechanism:**

Silicon forms strong covalent bonds with metals, while entropy stabilization reduces phase separation.

*Table: 1*

Ceramic Family	Examples of HECs	Crystal Structure
Oxides	(Mg,Co,Ni,Cu,Zn)O	Rock salt
Carbides	(Hf,Ta,Zr,Nb,Ti)C	FCC
Nitrides	(Ti,Zr,Hf,Nb,Ta)N	FCC
Borides	(Hf,Zr,Ti,Ta,Nb)B <sub>2</sub>	Hexagonal
Silicides	Multi-element silicides	Tetragonal

## PROCESSING AND SYNTHESIS METHODS OF HIGH ENTROPY CERAMICS (HECS)

The fabrication of High Entropy Ceramics is significantly more challenging than conventional ceramics due to the **need for homogeneous distribution of multiple cations** and the **requirement of single-phase stabilization**. The synthesis method strongly affects **phase formation, microstructure, density, and mechanical properties**. Various processing techniques have been developed and optimized depending on the **ceramic type (oxide, carbide, nitride, and boride)**, particle size, and intended application.

### 1. Solid State Reaction (SSR)

#### Principle:

In solid-state reaction, individual powders of constituent oxides, carbides, or nitrides are mixed in equimolar ratios and subjected to **high-temperature sintering** to induce diffusion and reaction, forming a single-phase HEC.

#### Steps:

1. **Powder weighing** according to target stoichiometry.
2. **Ball milling or manual mixing** for uniformity.
3. **Cold pressing** into green pellets.
4. **High-temperature sintering** (e.g., 1600–2200°C) in controlled atmosphere.

#### Advantages:

- Simple and cost-effective
- Applicable to large batch processing
- Works for most oxide and carbide HECs

#### Limitations:

- Long sintering times required (10–20 hours)
- Incomplete homogenization may lead to **secondary phases**
- Grain growth can be excessive, reducing mechanical properties

#### Example:

- (Mg, Co, Ni, Cu, Zn)O HEC was synthesized using SSR with >95% single-phase formation after 24 hours at 1000°C.

## 2. Spark Plasma Sintering (SPS)

### Principle:

SPS, also known as Field-Assisted Sintering Technique (FAST), uses **pulsed DC current** through the powder compact under uniaxial pressure, generating **Joule heating** internally, which accelerates densification.

### Steps:

1. Load mixed powders into graphite die.
2. Apply pressure (20–50 MPa) and pulsed DC current.
3. Heat rapidly (100–500°C/min) to sintering temperature (1600–2200°C).
4. Short dwell time (5–20 min) avoids excessive grain growth.

### Advantages:

- Rapid densification (minutes instead of hours)
- Fine and uniform microstructure
- Reduced porosity and enhanced mechanical properties
- Minimizes secondary phase formation

### Limitations:

- High equipment cost
- Limited sample size
- Graphite dies can react with some powders (carbides/nitrides)

### Example:

- (Hf, Ta, Zr, Nb, Ti)C HEC prepared by SPS showed **hardness of 35 GPa** and near-full densification within 10 minutes at 2100°C.

## 3. Mechanical Alloying (MA)

### Principle:

Mechanical alloying involves **high-energy ball milling** of powders to achieve **atomic-scale mixing** and induce solid-state reactions. It is often used as a precursor step before sintering.

### Steps:

1. Place powders in a planetary ball mill with milling media (e.g., steel balls).

2. Apply high-energy impacts for 10–50 hours.
3. Consolidate milled powders via SPS or hot pressing.

**Advantages:**

- Produces **nano-structured powders**
- Improves homogeneity and reduces sintering temperature
- Can induce **solid solution formation** during milling

**Limitations:**

- Long milling time may introduce contamination from milling media
- Agglomeration of fine powders requires careful handling

**Example:**

- Oxide HEC (Co, Ni, Cu, Mg, Zn)O was mechanically alloyed for 24 hours and then sintered via SPS, achieving single-phase rock-salt structure.

#### 4. Sol-Gel and Chemical Routes

**Principle:**

Chemical synthesis methods such as **sol-gel, co-precipitation, and combustion synthesis** produce HEC powders with **atomic-level homogeneity**, ideal for oxides.

**Steps (Sol-Gel):**

1. Dissolve metal precursors (nitrates, acetates) in solvent.
2. Mix with chelating agent (citric acid, ethylene glycol).
3. Heat to form a homogeneous gel.
4. Calcine at moderate temperature to form powders.
5. Sinter via conventional or SPS methods.

**Advantages:**

- Atomic-level mixing ensures **single-phase formation**
- Can produce **ultra-fine powders** (<100 nm)
- Better control of composition than SSR

**Limitations:**

- Not suitable for carbides or borides directly
- Organic residues require careful calcination
- Scale-up is more difficult and costly

**Example:**

- (Ce, Zr, Hf, Ti, La)<sub>2</sub>O<sub>3</sub> HEC synthesized via sol-gel method achieved **high surface area and uniform phase distribution**, useful for catalytic applications.

**MICROSTRUCTURAL CHARACTERISTICS**

HECs often exhibit:

- Single phase structure confirmed by XRD
- Uniform grain distribution
- Severe lattice distortion
- Low diffusion rate at high temperature

**MECHANICAL PROPERTIES**

HECs show remarkable mechanical performance.

*Table: 2*

Property	Conventional Ceramics	HECs/CCCs
Hardness	15–25 GPa	25–40 GPa
Fracture toughness	Low	Moderate improvement
Wear resistance	Moderate	Very high
Creep resistance	Limited	Excellent

**Reasons:**

- Lattice distortion
- Solid solution strengthening
- Grain boundary pinning

## **THERMAL AND CHEMICAL STABILITY**

HECs are highly stable at temperatures above 2000°C especially carbides and borides.

Oxidation resistance is improved due to formation of complex oxide layer. Sluggish diffusion prevents grain growth and phase transformation at elevated temperature.

## **FUNCTIONAL PROPERTIES**

### **1. Electrical Conductivity**

Carbide and nitride HECs show good electrical conductivity useful for electrodes.

### **2. Thermal Conductivity**

Lower than traditional ceramics due to phonon scattering from lattice distortion.

### **3. Radiation Resistance**

HECs are promising for nuclear applications because defects recombine easily.

## **APPLICATIONS OF HECs**

*Table: 3*

<b>Application Area</b>	<b>Role of HECs</b>
Aerospace	Thermal barrier coatings, nose cones
Nuclear reactors	Radiation tolerant materials
Cutting tools	Wear resistant tips
Defense	Armor materials
Energy	Electrodes, fuel cells

## **COMPARISON WITH TRADITIONAL CERAMICS**

HECs outperform many traditional ceramics in extreme conditions. Their multi element nature provides combined benefits which single component ceramics cannot achieve.

## **CHALLENGES IN DEVELOPMENT**

Despite advantages, HECs face issues:

- Difficulty in powder mixing
- High cost of raw materials
- Limited understanding of phase formation

- Scaling up for industrial production
- Lack of standard data

### **FUTURE RESEARCH DIRECTIONS**

- Development of lightweight HECs
- Additive manufacturing of HEC components
- Study of long term oxidation behavior
- Modeling and simulation for phase prediction
- Use in hypersonic vehicles

### **CONCLUSION**

High Entropy Ceramics and Compositionally Complex Ceramics represent a new frontier in advanced materials research. By combining multiple principal elements into a single phase ceramic structure, these materials show extraordinary mechanical, thermal and chemical stability. Their potential in high temperature and extreme environment applications make them very attractive for future technologies. However, more research is still needed to understand their thermodynamics, processing and large scale manufacturing. With continuous development, HECs are expected to replace many conventional ceramics in demanding applications.

### **REFERENCES**

1. Rost, C.M. et al., "Entropy-stabilized oxides", Nature Communications, 2015.
2. Gild, J. et al., "High-entropy ceramics: An emerging class of multicomponent materials", J. Eur. Ceram. Soc., 2018.
3. Sarkar, A. et al., "High entropy oxides for reversible energy storage", Nat. Commun., 2018.
4. Castle, E. et al., "Processing and properties of high entropy carbides", Scientific Reports, 2018.
5. Zhou, Y. et al., "Thermal stability of high entropy ceramics", Ceramics International, 2019.
6. Oses, C. et al., "High entropy ceramics: Review of principles", J. Mater. Res., 2020.
7. Wang, Y. et al., "Mechanical behavior of multi-principal element carbides", Acta Materialia, 2020.

8. Tallarita, G. et al., “Radiation tolerance of entropy stabilized oxides”, Scripta Materialia, 2019.
9. Feng, L. et al., “Oxidation behavior of high entropy borides”, J. Am. Ceram. Soc., 2021.