

Title: Synthesis of far-from-equilibrium materials for extreme environments

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Abstract

The search for materials that meet the contemporary engineering challenges, including the harsh environment of Generation IV nuclear reactors and the ultra-high temperatures in hypersonic vehicles, requires the exploration of structures only found beyond those achieved through conventional synthesis and processing techniques. These far-from-equilibrium materials are achievable through the application of one or multiple coupled extreme environments, allowing the systems to be kinetically trapped, or meta-equilibrated, in unique conditions across several length scales during processing. Here, we provide an overview of how coupled extreme environments, such as high temperature, high load or shear, irradiation and oxidation, may lead to the formation of materials with unique hierarchical microstructures with tolerance to harsh conditions beyond the capabilities of conventional materials. We discuss fundamentals, challenges, and opportunities of unprecedented performances for metals, oxides, and boride ceramics highlighting the distinctive characteristics that make these far-from-equilibrium materials exceptional for use in fields where multiple extreme conditions are met, such as the aerospace, nuclear energy, and energy storage applications.

Introduction

The most extreme of environments, such as combinations of high pressures and temperatures or irradiation and corrosive environments, can quite literally make or break a

material. While these conditions are typically seen as challenges to the traditional classes of materials, leveraging these environments during processing can unlock material structures and properties not feasible via conventional techniques. Extreme operating conditions are becoming commonplace as all areas of engineering design push the envelope on capabilities, whether that be aerospace vehicles with speeds beyond Mach 5, vehicles with reduced emission, or materials for Generation IV nuclear reactors. The requirements on the materials are pushed past the limit of existing traditional compositions and processing techniques. Rather than attempting to make incremental improvements using existing materials and or processes, one must shift the paradigm and consider avant-garde options. Oftentimes, drawing inspiration from outside fields can yield new perspectives previously not considered. **Figure 1** highlights some extreme processing conditions (e.g. pressure, shear, etc.), that when applied as coupled stimuli, lead to far-from-equilibrium structures achieving unprecedented properties. The coupling of stimuli during processing enables unique structures that outperform those achieved for the same compounds and chemistries produced by conventional routes.

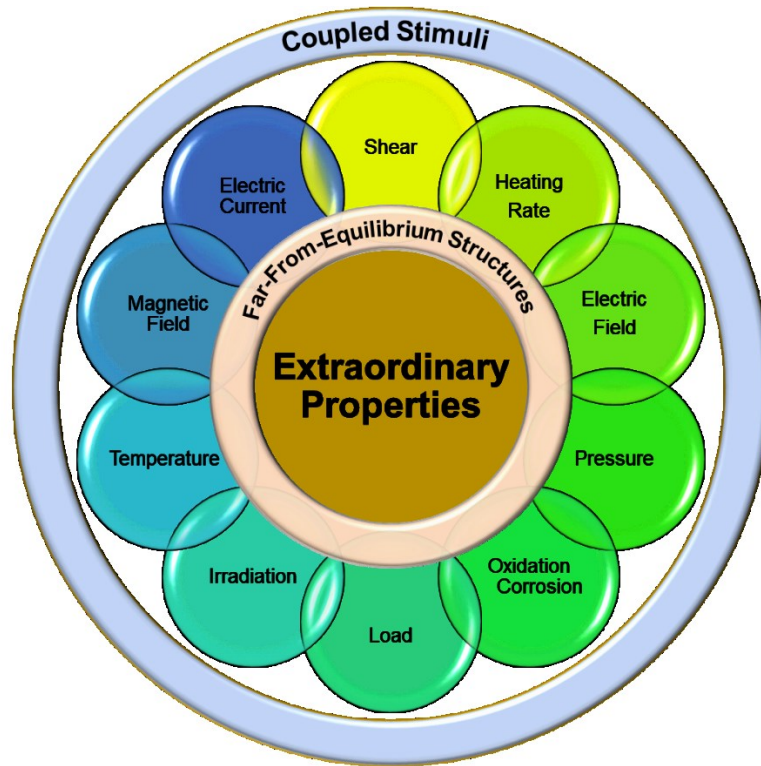


Figure 1. Extreme processing conditions that, especially when coupled, act as stimuli and lead way to far-from-equilibrium structures with extraordinary properties that enable survival during extreme operating conditions.

Here, we highlight several techniques for harnessing *coupled extreme processing stimuli* to create next generation materials for *coupled extreme environment applications*. First, we discuss the use of coupled extreme processing stimuli, namely high pressure and temperature particle/electromagnetic irradiation, to create metastable ceramic oxides with new compositions not possible using conventional techniques. These compositions are profitable, for instance, in the development of radiation tolerant structures, thermo-mechanically robust systems, and materials with controlled interfaces for maximization of ionic conductivity. Next, we look outside of traditional melt-processing techniques used for metallic alloys to solid-state routes to exploit the potential of non-equilibrium synthesis pathways to produce alloys and components with significantly improved performance for extreme environment applications, such as advanced

nuclear reactors and extreme temperature heat exchangers. Along the same theme of exploiting expertise from other fields, next we discuss the concept of adapting typical metallurgical techniques, such as work-hardening, to the ceramics field to create new uniquely tailored microstructural features in ultra-high temperature ceramics (UHTCs). These new microstructures ultimately result in significant enhancement in the thermo-physical and engineering properties *in-situ* during operation under extreme environments. These types of extreme thermal and mechanical environments are common for next generation aerospace vehicles due to the faster speeds and sharper leading edges over previous iterations, leaving few material systems that can survive. Beyond the use of the novel microstructures, we also present the concept of utilizing so-called ‘high entropy’ to stabilize new ceramic compositions that have shown promise to withstand these coupled extreme environments. The following sections aim to give a snapshot into each of these emerging fields in novel material synthesis for metallic and ceramic materials.

Accessing Singular Metastable States in Ceramic Oxides

Extreme processing stimuli (e.g., high temperature, high pressure) can lead to unparalleled evolution in materials, enabling access to unexplored microstructures with a multitude of technological opportunities. These far-from-equilibrium states represent unique structures at different spatial and temporal scales, achieved through energetic stimuli and management of kinetic traps to maintain the atomic configurations.^{1,2} A classical analogy is matter evaporation leading to unique arrangements of atoms as deposition occurs. Tailoring with temperature and pressure, the chemical potential of the vapor and its interactions with the substrate lead to controlled interfaces with unusual magnetic domains.³ The exposure to *extreme* processing stimuli (e.g. pressures above 10 GPa,⁴ temperatures beyond 2000 °C,⁵ or particle/electromagnetic irradiation⁶) coupled with other extreme-to-moderate stimuli vastly expands the materials’ energy and microstructural landscape. For example, stabilization of the

desirable radiation tolerant ortho-II phase in ZrO_2 requires the simultaneous application of multiple stimuli (i.e., pressures beyond 30 GPa and swift heavy ion irradiation).⁷ Without such coupled extreme processing stimuli, the ortho-II ZrO_2 reverts back to its monoclinic form when the singular stimuli of pressure is removed. The ability to stabilize non-equilibrium phases, such as ortho-II ZrO_2 , using coupled stimuli, further enables development of materials for extreme operating conditions by affording access to unique phases, microstructure, and compositions that were previously unattainable.

The stabilization of non-equilibrium states is analogous to the concept behind the Monte Carlo Method, in which unique metastable states can only be accessed if one surpasses confining parametric conditions, commonly found in regular processing conditions. While most of the energy landscape of two or more extreme stimuli is still unexplored (**Figure 2**), due to challenges in performing some of the required experiments, the existing studies offer encouraging results and demonstrate unique materials' properties. Take for example the stability of nanostructured oxides. Although such materials are known to be unstable with respect to bulk structures, a combination of high heating rates, pressure, and thermochemical design can enable the (meta)stabilization of these nanomaterials.⁸ Under pressure provided by, for instance, High Pressure Spark Plasma Sintering (HPSPS), the particles are forged together to create nanoceramics (i.e. nanocrystalline dense oxides).^{9–12} These structures still possess excess energy emerging from the grain boundaries, but by adding to the process the thermo-chemical design of interfaces, one creates a unique metastable nanoceramic, as demonstrated in Gd-doped ZrO_2 .⁸ Despite the nano-dimension, the Gd ions segregated to grain boundaries reduce the local excess energy, reducing the energy of this state to stabilize the nanoceramic.⁸ New proposed nano-scale diagrams aim to predict such nano-scale metastability landscapes, but efforts are still limited.^{13,14} From a processing perspective, only the usage of coupled extreme processing stimuli allows us to manufacture metastable dense nanostructures in ceramics.

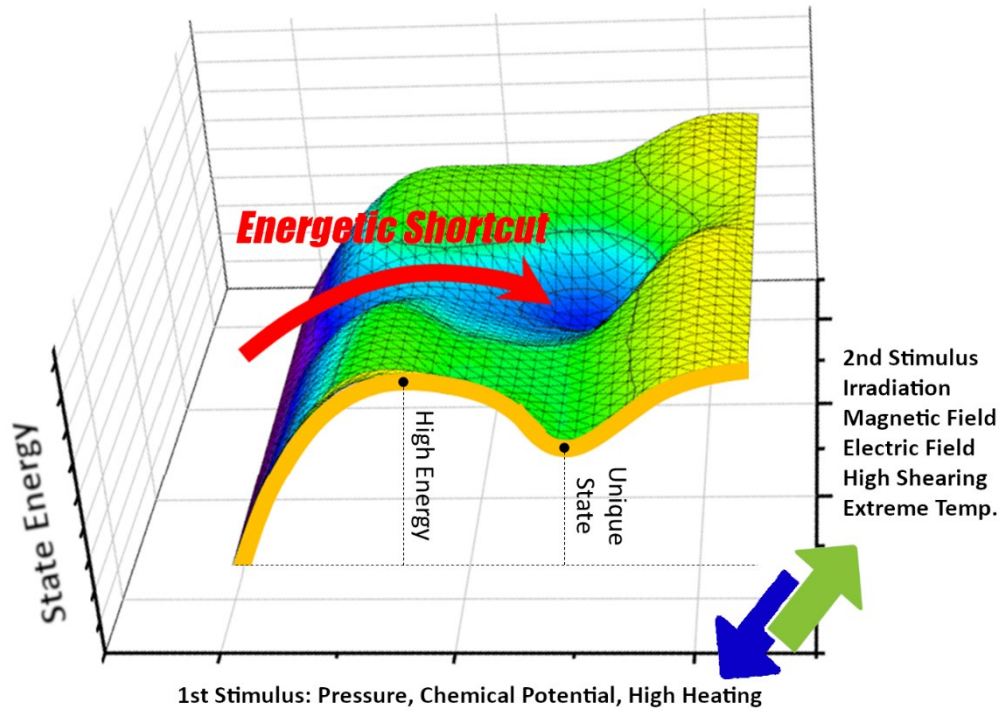


Figure 2. Broad energy landscape of materials, including exotic phases and other metastable structures, can be achieved through coupled extreme processing stimuli creating an energetic shortcut. These states are metastable though stable enough to be technologically exploited.

While the benefits of HPSPS have been attributed to high pressure and high heating rates, other field-assisted processes, such as flash-sintering and direct current sintering,^{15,16} offer additional opportunities in achieving unique atomic configurations, particularly at interfaces. Grain boundaries in oxide materials are known to develop space charge layers, through processes such as the spontaneous segregation of cations, that create electrical potential dwells and, in turn, compromise ionic conductivity.¹⁷ While dopants can partially mitigate this chemical/energy discontinuity, the combination of high heating rates ($> 500 - 1000$ °C/min) and electric field (> 1000 V/cm), in the absence of current, can modify the distribution of ions at the grain boundary region in complex oxides.¹⁸ For MgAl_2O_4 , which exhibits an accumulation of Al at the interfaces, electric fields under rapid sintering conditions can flatten out the Al-excess, as seen in **Figure 3**, mitigating the negative impacts of chemical/energy discontinuity.

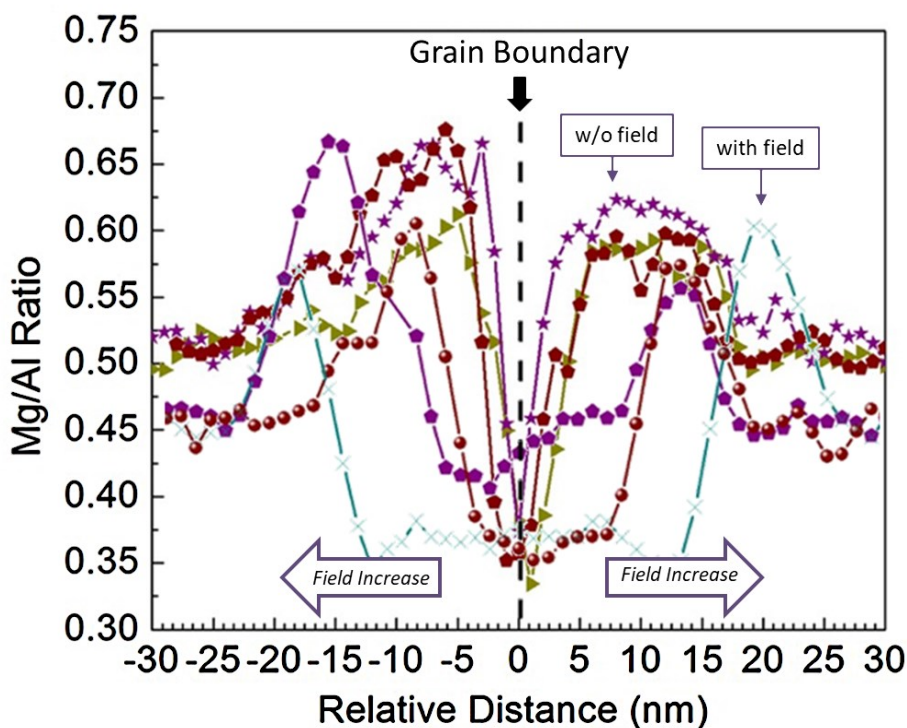


Figure 3. Distribution of Mg/Al across a grain boundary interface in MgAl_2O_4 crystals. Annealing at 1300°C combined with a second stimulus from a high electric field leads to a shift of the Mg/Al spatial distribution, modifying interfacial properties. Figure modified from Rufner et al. 2016.¹⁸

Application of high electric fields combined with moderate temperatures ($<1300^\circ\text{C}$) can also lead to the formation of an avalanche of defects in ceramics, making numerous desirable properties newly accessible at room-temperature. If electrodes can electrochemically interact with the ceramic and a current path exists, defect motion following the applied potential leads to bulk joule heating which eventually lowers the dielectric breakdown point and causes high current throughout the material which can enable rapid sintering.¹⁹ This process is known as ‘flash-sintering’, and despite the enormous challenges in obtaining homogeneous “conventional” ceramic compounds with this process, the large potential of ‘flash-sintering’ lies within creating far-from-equilibrium structures. Those structures containing defect pathways could, for example,

direct defect cascades in nuclear components for a controlled and more predictable damage profile, or amplify ionic conductivity in solid electrolytes for next generation solid-state batteries.²⁰

Although oxides were the first compounds ever used by humankind to solve an engineering goal, the application of coupled extreme stimuli during processing brings exciting new routes for promoting unexpected properties even in well-known compositions. While some of these far-from-equilibrium states are still only a scientific curiosity, the multiverse of properties opens unique opportunities in materials engineering. ‘Trapping’ the excited state so it survives target applications, particularly when dealing with coupled irradiation/pressure conditions, still requires extensive research. However, success cases, such as the design of meta-equilibrated nanoceramics with unique mechanical properties and high thermal stability through application of coupled extreme processing stimuli, encourage the continued research seeking unique far-from-equilibrium microstructures for coupled extreme environment applications.

Solid phase processing of metal alloys and composites

Parallel to oxides, the production of next-generation transformative metal alloys and composites at scale relies on the development of synthesis methods that circumvent the historic constraints on chemistry and structure imposed by *melt-based* processing approaches and exploit the potential of non-equilibrium synthesis pathways to produce materials and components with significantly enhanced performance. For example, while extreme pressures (> 50 GPa) produce unique properties in some metals, such as a lowering of the magnetic ordering and enabling superconductivity,²¹ these properties cannot yet be sustained once pressure is removed, nor can they be produced at bulk scale. However, as with ceramics, a combination of stimuli during synthesis has the potential to not only reduce the energy demand for processing of metal alloys to meet conventional engineering standards, but also lead to the discovery of metastable states with unprecedented properties. A key example is through the application of a high shear strain during synthesis and/or fabrication, creating a mechanical-thermal coupling that facilitates

diffusional processes and phase transformations within a metal alloy or composite to produce high-performance microstructures without the need to melt the starting materials, as seen in **Figure 4**.

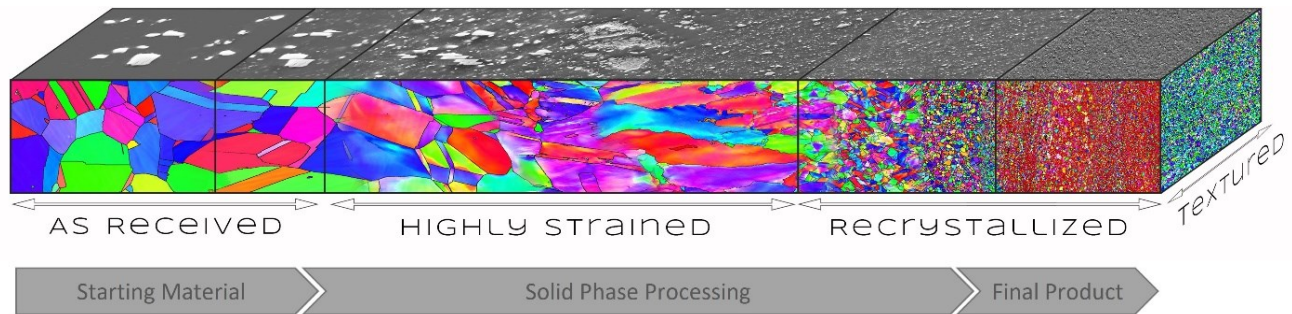


Figure 4. Solid Phase Processing (SPP) methods use the application of a high shear strain to create metal alloys and composites and engineered components, without the need to melt the constituent materials.

This manufacturing approach, known as Solid Phase Processing (SPP), was first introduced in the 1980s as a thermal spray coating technology called cold spray¹ and extended to metals joining in the early 1990s with Friction Stir Welding (Mishra & Ma, 2005). In the subsequent decades, additional SPP approaches have been developed, including Friction Stir Processing,² Friction Extrusion,^{3,4} Shear Assisted Processing and Extrusion (ShAPE),^{5,6} Friction Consolidation,⁷ and Friction Stir Additive Manufacturing.^{8,9} All of these methods have been demonstrated to produce improved, and sometimes dramatically improved, performance in metal alloys and components relative to the same products produced by conventional melt-based processing methods. Because synthesis occurs wholly in the solid phase, SPP methods can enable the scalable synthesis of metal alloys and composites that are difficult-to-impossible to produce via conventional melt-based processing methods due to chemical incompatibilities in the melt, or the formation of deleterious intermetallic second phases upon cooling, leading to the

potential for the production of entirely new families of metal alloys and composites. In addition to the potential to deliver new metal products with extraordinary performance, SPP methods can also enable significant process intensification during metals manufacturing, with the potential to be less energy intensive, with a smaller carbon footprint and lower cost, than conventional metals production pathways.

Three key characteristics are common to most SPP methods:²²

- The thermal energy required for material mixing and flow is generated by the high-strain through an adiabatic heating effect, introduced by the high-strain-rate deformation that results from the process itself, which can reduce or eliminate the need for external heating of the materials and/or tools. The process can produce so much heat that cooling is needed to maintain synthesis in the solid phase.
- The large shear strains introduced in relatively small volumes of material during SPP activate a combination of enhanced diffusion and advection processes within the evolving metal alloy.
- During SPP, only a relatively small volume of material is shear-processed at any one time, facilitating the rapid heating and cooling of the processed region, and reducing the energy inputs required during manufacture.

Combined, these characteristics of SPP also offer a pathway to an exciting new regime of scalable, far-from-equilibrium metals synthesis in which final microstructures—and thus, properties and performance—are defined not just by equilibrium thermodynamics, but also by the kinetics that are active in the solid phase.^{10–15}

SPP methods are already providing scalable pathways to high-performance metal alloys and composites, as well as finished and semi-finished high-performance metal components, for

a variety of applications that will help to enable the Department of Energy's (DOE) goals for a net-zero emission economy by 2050.²³ For vehicle light-weighting, friction stir welding is used to produce tailor-welded blanks of dissimilar aluminum alloys that are strong enough to survive stamping into parts for the automotive industry;¹⁶ this process is now commercially implemented in a number of United States manufactured cars and trucks, including the Ford F-150. Other solid phase processing methods like ShAPE have demonstrated the production of aluminum^{17,18} and magnesium alloys⁶ with improved strength and ductility relative to identical alloys produced by conventional means, providing pathways for additional vehicle light-weighting while also reducing the carbon-intensity of manufacturing through process intensification. Direct recycling of 100% 6063 aluminum scrap to high-performance products with applications targeted for electric vehicles has also been recently demonstrated via a ShAPE process that is now being scaled up for commercial implementation.²⁴ Because this SPP approach to recycling does not require the addition of virgin aluminum to achieve requisite product performance, the carbon emissions associated with the recycled aluminum product reduce by more than 90%.

The advantages of SPP approaches to metal alloy and composite synthesis are not limited to improvements in mechanical properties for structural applications. SPP methods (e.g., friction extrusion and ShAPE) can also deliver improved performance in functional materials, where a refined microstructure, including a desired texture, has been demonstrated to provide a decreased coercivity in soft magnets¹⁹ and improved transport properties in BiTe thermoelectrics.²⁰ The homogeneous distribution of very small amounts of graphene in copper²¹ and aluminum alloys leads to increases in electrical conductivity and, more important to many energy applications, a decrease in the temperature coefficient of resistance, while also improving the strength and ductility of the composite. Finally, SPP is a demonstrated pathway to manufacture components for use in extreme energy environments: friction stir welding provides joints in ferritic steels with creep resistance equivalent to the base metal for heat-exchanger applications, and can also be used to repair damage due to stress corrosion cracking in dry

storage casks for spent nuclear fuel rods. Early research suggests that ShAPE can provide a pathway to fully-dense radiation resistant oxide-dispersion strengthened ferritic alloy claddings for the nuclear industry.^{7,22}

To date, much of the research and development of SPP methods has focused on the synthesis and fabrication of metal alloys that were originally designed for manufacture by conventional melt-based processing methods. While these SPP approaches continue to deliver improved products relative to conventional manufacturing, the full potential of solid phase processing has yet to be explored. As scientists develop a more complete and predictive understanding of process-structure relationships in metals exposed to the high shear strain that is common to solid phase processing methods, and as engineers learn how to better sense and control synthesis conditions during SPP, the opportunity will exist to design entirely new metal alloys and composites that fully exploit synthesis in the solid phase. This will enable scalable production of far-from-equilibrium materials that exhibit combinations of properties that have yet to be measured, for applications that have yet to be imagined.

Strain hardening of ultra-high temperature ceramics upon exposure to extreme environments

Though exploitation of typical metallurgical processes like work hardening, alloying, or thermal treatments (i.e., annealing, quenching, tempering) enable property improvements in metals, the same principles have yet to be fully exploited for ceramics. In cases where these processes have been explored, ceramic materials exhibit significant improvements in performance. For instance, the development of uniquely tailored microstructural features ultimately result in significant enhancement in the thermo-physical and engineering properties when utilized under coupled extreme environments of temperatures above 1600°C and high mechanical loads over 600 MPa.²⁵ This is the case for ultra-high temperature ceramics (UHTCs), a class of materials including borides, carbides, and nitrides that have some common features,

including directional covalent bonding and high modulus ($\sim 500\text{GPa}$)²⁶ combined with melting point above 3000°C . As such, the sintering of UHTCs requires high temperature and pressure.²³ Materials synthesis in such extreme conditions often leads to grain coarsening or trapped porosity, both of which are detrimental to the mechanical properties. However, a relatively simple route that uses powder milling and sintering enables production of bulk UHTCs with full density and mean grain size in the $1\text{-}2\ \mu\text{m}$ range that exhibit a singular microstructure organized in a hierarchical fashion on multiple length scales, with nano-sized inclusions of variable nature, either metal or even boride and carbide.^{24,25} So far, the main obstacle to fabricate ceramic/metal nanocomposites has been the handling of nanometer size particulate systems,²⁶ but this harmful step can be skipped by taking advantage of the solid solution principles of dissolution, super-saturation, and precipitation. This will reduce the cost and risk factors involved in the whole industrial process associated with the production of nano-UHTC composites.

A fundamental attribute for the development of a hierarchical structure in most UHTCs is a mobility of the relevant transition metals and solubility within the hosting cell. Sintering of borides and carbides at high temperature in the presence of another transition metal (TM) (i.e., guest metal), leads to the formation of a particular grain configuration, known as “core-shell” or “core-rim,” **Figure 5**. The core is the original grain, and the shell is a solid solution, epitaxially-matched around it that contains different amounts of the guest metal depending on its solubility within the boride or carbide lattice. At the interface between the two regions, dislocations are created by accommodation of the elastic constants mismatch upon cooling.²⁷ Using appropriate composition, consolidation, or post-thermal treatment conditions, the shell morphology can be manipulated (i.e. enlarged or super-saturated) thus triggering the precipitation of nano-inclusions.²⁵ These precipitates form within the boride grains and result in a hierarchical UHTC-TM hybrid structure consisting of homogeneously distributed nano-sized inclusions embedded into micron-sized grains. The hierarchical structure, already demonstrated in the case of ZrB_2 ^{28–30} and HfB_2 ²⁴ sintered in presence of W- or Ta- compounds, offers benefits in terms of preserved grain size,

significant plastic deformation by dislocation movement, increased local fracture toughness through the presence of ductile inclusions, and the ability to maintain strength in the ultra-high temperature regime by strain hardening.²⁵ As such, improvements of mechanical properties by incorporation of dispersed metal nano-particles (e.g., W, Mo, Ni, Al,) to a ceramic matrix had been successfully applied in oxide-based systems (mullite/Mo,³¹ $\text{Al}_2\text{O}_3/\text{Ni}$,^{32,33} $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{Ni}$ ³⁴) and more seldom in nitrides (AlN/Mo , AlN/Al),^{35,36} with particular benefits on the fracture toughness. Remarkably, most of the property improvements have been achieved upon introduction of low to moderate volume fractions of metal. An exact measure of the inclusions precipitating in boride grains upon exposure to high temperatures has not yet been possible, due to issues encountered in actually identifying the inclusions. In fact, inclusion identification has only been achieved thus far on the fracture surface by SEM, or on thin specimens by TEM. However, this concept supports the premise that there exists a specific amount of inclusions required to achieve beneficial properties in materials, such as oxide-nitride based systems, and may extend the performance of UHTCs if further explored and adopted.

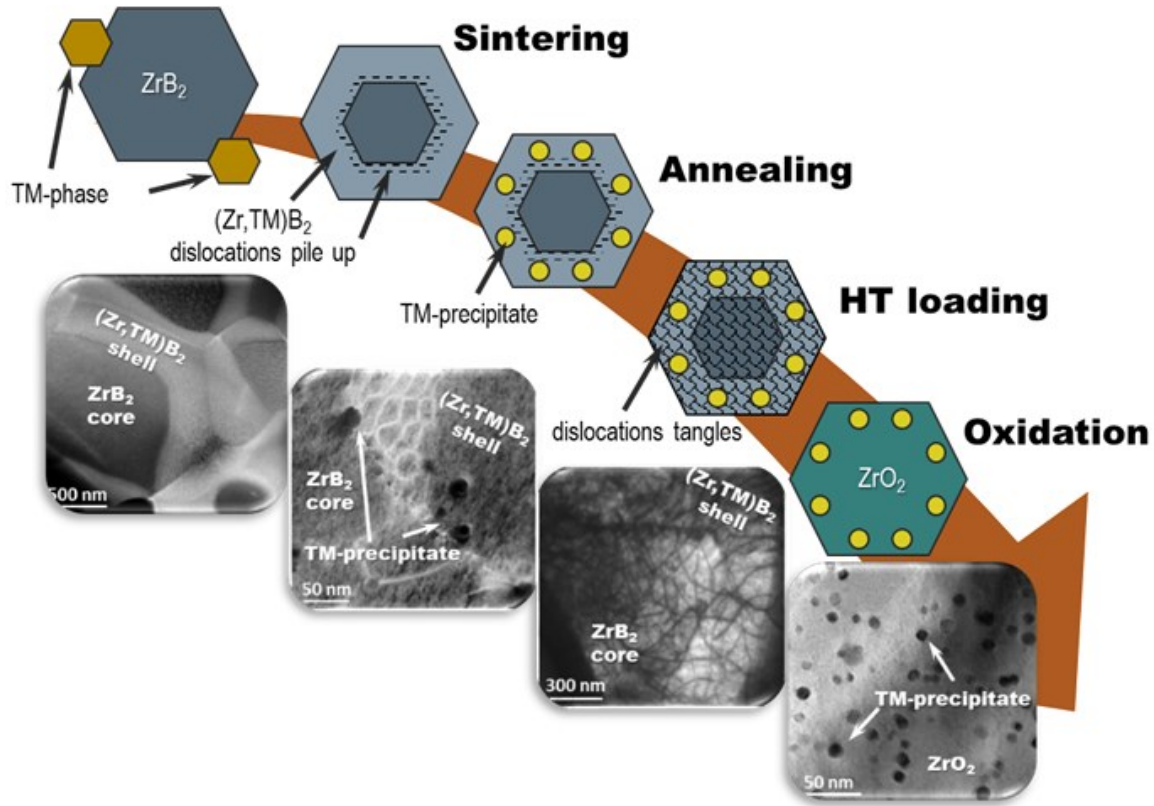


Figure 5. Schematic of the microstructure evolution from raw micron-sized powder to a hierarchical multi-scale configuration, passing through the core-shell structure, and upon exploiting the application of high temperature during sintering and annealing, high temperature loading, and oxidation. Below the orange arrow, transmission electron micrographs capturing the main morphological features.

One of the most recent achievements was a strength increase in a $\text{ZrB}_2\text{-WC}$ system, which passed from 600 MPa strength at room temperature to 1 GPa at 1800°C, remained over 800 MPa at 1900°C and did not exhibit catastrophic failure but bent at 2000°C, due to the ductility of some secondary phases and the approach to eutectic temperatures in the system.²⁵ These strength limits, which surpass current state-of-the-art strengths by more than 700 MPa at such temperatures,^{37–39} can be further pushed to higher temperatures by decreasing the amount of WC and thus inducing a plastic behavior beyond 2100°C.²⁸

While the core-shell grain morphology overcomes the challenges encountered when materials are exposed simultaneously to the coupled extreme environments of temperature and mechanical load, this hierarchical structure also provides benefits against even more challenging coupled extreme environments.^{40–42} For instance, adding oxygen or dissociate species results in nested nano-inclusions that remain well protected within the boride grains, **Figure 5**, that instead oxidize into more desirable zirconia or hafnia. These nano-inclusions therefore continue to exert their function of local toughening and strain hardening even when they are subjected to hypersonic conditions of 2400 - 2550 °C peak temperatures and oxygen partial pressures in the order of tens to thousands of pascals.⁴³

Further, new challenges and opportunities are now open for the development of novel multi-scale nano-structured composites with enhanced behavior not just from a thermo-mechanical standpoint. Indeed, similar procedures could be extended to other materials systems with possible benefits to other materials properties. For instance, hierarchical nanocomposites were previously studied for their anomalous super-hardness.⁴⁴ These discoveries represent the first step toward the understanding of the underpinning mechanisms that govern the significantly improved properties in high entropy ceramics (HECs) that display hardness well beyond that of the constituent pure compounds.^{45,46} Indeed, adding at least five transition metals into boride or carbide matrices to produce HECs is likely to promote precipitation of nano-inclusions, as observed for high-entropy metal alloys, where ultra-high strengths were attributed to the precipitation strengthening afforded by intragranular nano-inclusions in a primary phase.^{47,48}

These recent findings tackle some contradictory aspects, whose coexistence looks impossible according to the laws of physics. However, we might actually be on the right path towards the solving of the strength and toughness paradox,⁴⁹ particularly within coupled extreme environments, while still exploiting simple and scalable synthesis and processing routes.

Processing and properties of high-entropy ultra-high temperature ceramics

Although application of the high-entropy design concept has led to improved properties of metallic alloys in extreme environments (e.g., cryogenic temperatures²⁷ and irradiated conditions²⁸), translation of this concept from metallic to ceramic materials has been slow. While the first high-entropy metallic alloys appeared in 2004,^{29–31} only recently has the high-entropy design concept been applied to bulk, monolithic ceramic materials (the first instance appearing in 2015),³² including oxides,^{32–35} silicides,^{36,37} borides,^{38–40} and carbides.^{41–43} For example, a high-entropy boride (HEB) is provided in **Figure 6c**, where the HEB exhibits a hexagonal crystal structure with the metal atoms randomly intermixed on cation lattice sites (M_1 to M_5) to form a random solid solution with the rigid two-dimensional boron net on the adjacent lattice plane.³⁸ Through the high-entropy design concept, chemical composition can also be used to extend phase space beyond prevalent binary or ternary compounds to quaternary and quinary compositions. By increasing the number of principle elements well beyond the number of crystal compound structural sub-lattices, chemistry serves as an internal stimulus to extend the equilibrium composition of a crystal structure well beyond currently perceived limits, **Figure 6a-b**. Many ceramic materials do not exhibit explicit “high-entropy,”⁴⁴ (**Figure 6d**), so classifying these materials as complex concentrated or multi-principal element compounds may be more appropriate.⁴⁵ This brings the focus back to the design of materials systems with high concentrations of multiple elements to achieve desired properties and allows for inclusion of non-equimolar materials systems with low or medium entropy. Nevertheless, the term ‘high-entropy’ remains due to its recognition and prevalence in the field.

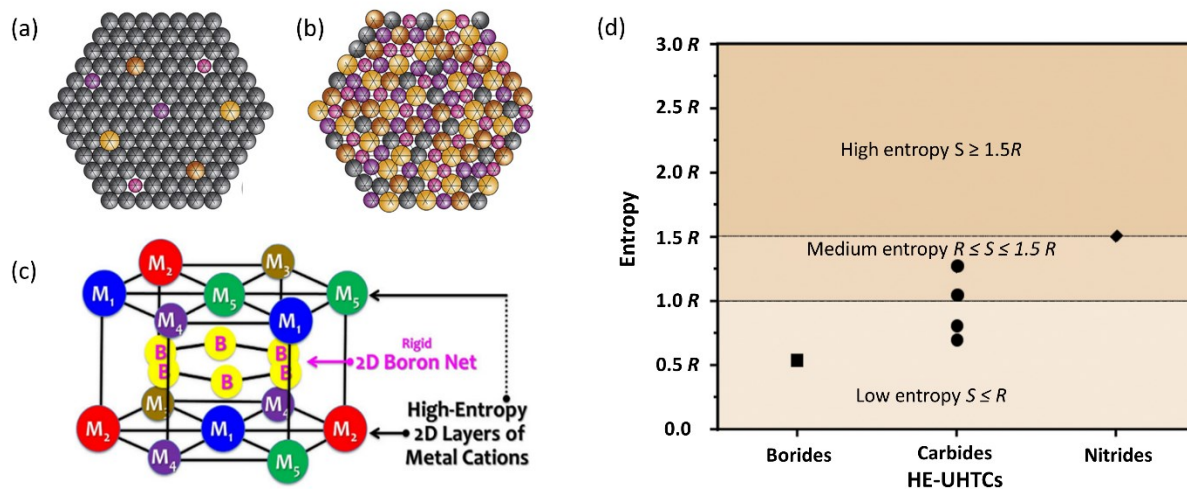


Figure 6. (a) Schematic of doping a materials system with minor amounts of elements (orange, yellow, purple) that differ from the major element (gray).⁴⁶ (b) Schematic of complex concentrated (e.g., high-entropy) materials where all elements (orange, yellow, purple, gray) are present in high concentrations.⁴⁶ (c) Schematic of high-entropy boride (HEB), where a random solid solution of metal atoms ($M_1 - M_5$) on the hexagonal crystal lattice surrounds the two dimensional net of boron atoms (B).³⁸ (d) Classification of high, medium, and low entropy based on the magnitude of the idealized configurational entropy (S) for selected 'high-entropy' borides, carbides, and nitrides, where R is the gas constant.⁴⁴

Here, the focus is on high-entropy borides (HEBs) due to the higher thermal conductivity and temperature stability over carbides, making them more attractive for coupled extreme environment applications, such as leading edges in high-speed flight (i.e., temperatures >2000 °C and heat fluxes ~ 1000 W/cm²).^{47–49} Although HEBs offer promising performance, non-optimal processing conditions lead to the formation of secondary phases and defects that impact mechanical properties and performance within extreme operating conditions. Therefore, careful consideration of the processing space is required as the phase stabilization greatly depends on the stimuli applied during processing.

Typically, HEB precursor powders are fabricated into bulk samples by mechanically mixing/alloying the powder followed by densifying the powder using coupled extreme processing stimuli (e.g., high temperature and high pressure during spark plasma sintering).^{50,51} While there is not yet a dominant processing route used to make bulk HEBs, these samples are commonly prepared through reaction of (1) metal diboride powder, (2) metal powders with a boron and carbon source, or (3) metal oxide powder with a boron and carbon source. Finer powders improve sinterability, and, as a result, a controlled inert atmosphere is required to reduce flammability of very fine (typically nanometer-sized), pyrophoric, precursor metallic powder. As an alternate approach, the borocarbothermal reduction processing route employs metal oxide precursor powders, along with a boron and carbon source, reducing the need for highly controlled powder handling protocols. However, multiple high temperature processing systems are usually required to prepare HEBs from borocarbothermal reduction since lower temperature reactions (e.g., boria off-gassing or borocarbothermal reduction) are difficult to accommodate in the same system that can produce the coupled extreme processing stimuli.⁴⁵ In cases where a single high temperature processing system was employed, secondary boride and oxide phases were present while lower materials conversion rates and sample densities were produced, when compared with a multi-step processing route.⁵² Although excess boron and/or carbon are commonly added to reduce the oxygen impurities during processing,⁵¹ the use of multiple high temperature processing systems results in potential exposure to oxygen and increased safety risk, due to handling of pyrophoric powders. There has been some success in producing dense, nominally phase pure HEB samples using multi-step processing with coupled extreme processing stimuli. For instance, Reactive Flash Spark Plasma Sintering (RFSPS) couples applied voltage (50 – 150 volts)⁵³ and, in turn, extremely high temperatures (~3000 °C - 4500 °C) to produce dense, nominally phase pure $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2})\text{B}_2$ samples from binary metal diboride precursor powders.⁵⁴ Further exploration of coupled extreme external stimuli is recommended to overcome the processing challenges associated with preparation of novel high-entropy ceramics.

The high-entropy UHTC field has focused on improving extreme environment performance by modifying the composition to enhance tunability (i.e., number of design parameters versus the design constraints) of properties. Notable studies exploring the effects of composition on mechanical properties^{55,56} and oxidation^{57,58} have been pushing the high-entropy UHTC field in this direction. Complex oxide scale formation (i.e., oxides with 3 or more principal elements) has the potential to improve oxidation resistance over binary oxides.^{59,60} Specifically, the ability to design the composition of the oxide scale that forms during oxidation is desirable to improve oxidation resistance. Backman et al.^{57,58} showed that in the HEB system, $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2})\text{B}_2$, the group IV elements (i.e., Hf, Zr, Ti) will undergo preferential oxidation leading to a group IV-rich surface oxide that resides on top of a group V-rich boride. The higher melting temperatures of group IV oxides are desirable for designing a high temperature protective oxide scale for coupled extreme environment applications. Knowledge of preferential group IV element oxidation in HEBs is promising for the design of complex oxide scales with improved oxidation resistance for next generation high-entropy UHTCs.

Branching into exploration of non-equimolar compositions has the potential to balance materials properties to address competing design requirements in coupled extreme environment applications and push the high-entropy UHTC field towards designable complex oxide scales. For example, insights from Feng et al.⁵⁵ show that Nb-containing HEBs form Nb-rich secondary phases that suppress grain growth, leading to a reduction in grain size with increasing Nb content. Although reducing the grain size is beneficial for thermal shock resistance,⁶¹ Nb provides poor oxidation resistance, with the onset of oxidation occurring at lower temperatures (<500 °C).⁶² As such, minor additions of Nb to HEBs may help improve mechanical properties through grain refinement without diminishing the oxidation resistance. These studies promote further exploration of non-equimolar HEBs in order to balance competing design requirements by refining materials properties.

In addition to evaluating non-equimolar compositions, exploration of the phase space beyond high-entropy ceramics with group IV, V, VI transition metals has begun to include group III transition metals (i.e., rare earth cations). Qin et al.⁵⁶ demonstrated extended phase stability using the high-entropy design concept to incorporate rare earth cations into transition metal HEBs. That study is significant for two reasons, (1) rare earth oxides exhibit higher melting temperatures than some transition metal oxides⁶³ which could lead to higher oxidation resistance in HEBs, and (2) the ability to form a single phase within this extended compositional space (i.e., group III rare earth transition metals added to HEBs with group IV, V, VI elements) is more challenging and depends on the processing route used. Although the performance of single phase versus multi-phase HEBs has not yet been extensively studied, the work by Qin et al.⁵⁶ suggests that the ability to prepare single phase HEBs within an extended compositional space (e.g., group III – VI transition metals) depends on choosing an appropriate processing route.

While initial results from high-entropy ceramics garnered interest in the UHTC field, more work is needed to achieve wide-spread acceptance and implementation into extreme environment applications, such as high-speed aircraft. If high-entropy UHTC materials are to make their way to these applications, they would either need to be used as coatings or would need to see a substantial increase in mechanical performance, such as through fiber reinforcement. From a processing standpoint, application of coupled external stimuli during processing may enable such mechanical performance enhancements, though further exploration is needed.

Conclusions

New trends in material synthesis are rapidly evolving to meet the needs of coupled extreme environments encountered in the next generation concepts for the industries spanning aerospace, defense, and energy. Application of coupled extreme processing stimuli has been shown to provide promising routes to new material properties that were previously unachievable using traditional synthesis techniques. However, designing materials and experimentally

validating new materials for applications that experience multiple extreme environments remain challenging. Here we discuss current research thrusts that aim to address the challenges associated with coupled extreme environment applications, yet each new discovery results in more puzzling questions. In addition, further research is required to propel the field of designing materials for extreme environments forward. A few specific areas of interest include, (1) pairing computational materials discovery and simulated stimuli responses with laboratory experiments, (2) standardizing extreme environment tests, which are often limited to one stimuli at a time and therefore deviate from the application environment and make the creation of properties maps unfeasible, and (3) utilizing a holistic design approach to achieve a multi-faceted design view for producing sustainable novel materials with enhanced properties.

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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