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## INTRODUCTION

The original concept of entropically stabilized solid solutions proposed in 2004 has evolved into the development of high-entropy materials (HEMs), which include high-entropy alloys (HEAs) and high-entropy ceramics (HECs). These are multicomponent systems that occupy the uncharted regions of phase diagrams; they have become exciting and vibrant fields of research since the concept was first proposed. The distinguishing features of these multicomponent systems offer great potential in various fields, including structural materials, magnetic materials, thermal barrier coatings, thermoelectrics, catalysts, batteries, and coatings against wear and oxidation/corrosion. This special topic collection on the “Design and development of high entropy materials” is motivated by the continuous evolution and expansion of the field. The articles included in this collection provide a comprehensive overview of the field’s current state, from the recent progress in the oxidation behavior of HEAs to the thermal and mechanical properties of entropy-stabilized materials and the potential of HEMs in Li-ion batteries and other applications.

The collection includes a wide range of topics, from the fundamentals of HEMs, such as defining what constitutes a “high entropy” material, to cutting-edge research on novel applications, such as the development of ferromagnetic HEMs and the use of machine learning for inverse design of single-phase alloys. Other articles delve into the properties of various HEMs, such as their ideal simple shear strengths, magnetocaloric effects, and the role of secondary

phase formation in enhancing their functional properties. The collection also covers the synthesis and development of new HEMs, including bio-based alloys and high entropy borides synthesized via microwave-induced plasma.

## SYNTHESIS AND DESIGN

Storr *et al.*<sup>1</sup> report the synthesis of high entropy boride ceramics using microwave-induced plasma. Predominantly single-phase borides (Hf, Zr, Ti, Ta, Mo)B<sub>2</sub> and (Hf, Zr, Nb, Ta, Mo)B<sub>2</sub> with hexagonal ordering were prepared, and they showed an oxidation resistance that was improved by as much as a factor of 10 compared to conventional diborides. Simultaneously, the hardness of these materials was as much as 50% higher compared to other studies for the same chemical configuration and testing load. This study presents the potential of using microwave-induced plasma as a novel approach for synthesizing high entropy ceramics.

Anber *et al.*<sup>2</sup> examine the role of Al additions in the stability of the CoCrFeNi base alloy. The increase in the Al content stimulates the formation of NiAl-B<sub>2</sub> phase, increases the overall density of the secondary phases, and influences the composition of the Cr-rich BCC phase. The work provides a foundation for a predictive understanding of phase evolution, opening the window toward designing innovative alloys for targeted applications.

Zeng *et al.*<sup>3</sup> develop an inverse design framework to search for single-phase HEAs subject to specified phase targets and constraints. This framework is based on the fast grid search in the

composition–temperature space enabled by a highly accurate and efficient machine learning model. Using the framework, authors searched through the entire quaternary, quinary, and senary alloy systems formed by Al, Co, Cr, Cu, Fe, Mn, Ni, and Ti and identified three types of HEAs: (1) single-phase FCC HEA with the highest Al content; (2) single-phase FCC HEA with lower equilibrium temperatures; and (3) single-phase BCC HEA with Al as a principal element. All the designed HEAs were verified by the equilibrium calculations with Thermo-Calc software and TCHEA3 database.

Kim *et al.*<sup>4</sup> present an approach to increase the structural and compositional complexity in HECs, proposing guidelines to promote single-phase formation of HECs. This guideline identifies a critical dependence on the structure of the product HEC compared with its parent compounds. Based on the proposed empirical rules, a new type of high-entropy silicides with a B20 structure, (CrMnFeCoNi)Si, was developed. The single-phase region of the B20 silicide was further expanded from the (CrMnFeCo)Si pseudo-quaternary system to the (CrMnFeCoNi)Si pseudo-quinary system, providing a potential strategy to utilize multi-constituent cocktail effects in HECs with higher structural and compositional complexity.

## MECHANICAL PROPERTIES

Hsieh *et al.*<sup>5</sup> present the mechanical properties and microstructures of  $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$  after welding by gas tungsten arc (GTA) welding and friction stir welding (FSW). GTA welding of precipitated HEAs resulted in alloys with significantly decreased hardness and tensile properties compared to the base metal. HEAs synthesized using FSW exhibited excellent mechanical properties. Comparing the differences in the microstructure and mechanical properties between the two welding processes, the authors explain the reasons and mechanisms for this difference and identify FSW as a better welding method to precipitate high entropy alloys than GTA.

Xu *et al.*<sup>6</sup> present atomistic simulations of chemical short-range ordering in two body-centered cubic refractory multi-principal element alloys, HfMoNbTaTi and HfNbTaTiZr, and study its influence on their ideal simple shear strengths. Both the alias and affine shear strengths were analyzed on the {110} and {112} planes in the two opposing <111> directions. In both quinary alloys, local ordering of NbNb, TaTa, HfNb, HfTa, and NbTa was preferred as the annealing temperature was decreased. The pair that achieved the highest degree of local ordering was TiTi in HfMoNbTaTi and HfTi in HfNbTaTiZr. Subject to the affine shear, these alloys yielded by first phase transformation at the most likely pairs followed by deformation twinning at those sites.

Rost *et al.*<sup>7</sup> investigate the thermal and mechanical properties of the entropy stabilized oxide  $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$  across the boundary between “high-entropy” and “entropy-stabilized” phases. Its thermal conductivity remains constant within uncertainty above and below the transition, while the linear coefficient of thermal expansion changed by nearly 24%. Significant mechanical softening is also observed across the transition.

Fan *et al.*<sup>8</sup> report the mechanical properties of a novel high-entropy alloy ( $\text{Ni}_{25}\text{Cu}_{18.75}\text{Fe}_{25}\text{Co}_{25}\text{Al}_{6.25}$ ) using nano-scratching experiments and MD simulations. The joint experimental/computational effort investigates dislocation-mediated plastic mechanisms leading to side flow, pileup, and crystal defects formed

in the sub-surface of the HEA during and after the scratch process. Crystal defects associated with the plastic deformation of the face-centered cubic structure of the HEA are identified. The (100) orientation of the HEA is suggested to be better than the other orientations for improved contact-mode manufacturing.

Nutor *et al.*<sup>9</sup> report on the microstructure and tensile deformation behavior of the  $\text{Al}_7(\text{CoNiV})_{93}$  medium entropy alloy (MEA). Emphasis is placed on the high-temperature tensile behavior and the underlying microstructural evolution. The alloy showed a remarkably high tensile strength and good ductility. The strain rate sensitivity is found to be typical of alloys that show quasi-superplastic elongation. The inability of the alloy to access true superplasticity was attributed to immense cavitation due to the high amount of the brittle  $\sigma$  phase, which served as decohesion sites for the early fracture of the sample.

## MAGNETIC PROPERTIES

Kitagawa *et al.*<sup>10</sup> report the discovery of ferromagnetism in the cubic CsCl-type  $\text{Ti}_{21\sim 25}\text{Nb}_{20\sim 24}\text{Cr}_{5\sim 10}\text{Ru}_{\sim 49}$  multicomponent alloy. The ferromagnetic nature was confirmed by the isothermal magnetization curve. The authors further investigate the effect of elemental substitution on the ferromagnetic behavior. The partial substitution of Pd for Ru heavily suppressed the Curie temperature, indicating that the Ru atom may play an essential role in sustaining ferromagnetism.  $\text{Ti}_{21\sim 25}\text{Nb}_{20\sim 24}\text{Cr}_{5\sim 10}\text{Ru}_{\sim 49}$  would be the first example of ferromagnetic Cr-containing multicomponent alloys, and this study shows the usefulness of the large compositional space in exploring novel phenomena.

Guo *et al.*<sup>11</sup> present a six-component MnFeCoNiGeSi high-entropy system exhibiting a low-hysteresis magnetostructural transformation between ferromagnetic orthorhombic and paramagnetic hexagonal phases. The increase in configurational entropy achieved by adding Si and Fe motivates the transformation from a single hexagonal structure at high temperatures to the orthorhombic structure upon cooling. The obtained room-temperature magnetocaloric performance was comparable to that of some rare-earth-based high-entropy alloys and conventional first-order magnetocaloric materials.

Wang *et al.*<sup>12</sup> explore a family of compositionally complex cubic spinel ferrites with combinations of Mg, Fe, Co, Ni, Cu, Mn, and Zn cations. All compositions resulted in ferrimagnetic average structures with remarkably similar local bonding environments. However, the samples displayed varying degrees of cation inversion and, therefore, differing apparent bulk magnetization. Additionally, first-order reversal curve analysis of the magnetic reversal behavior indicated varying degrees of magnetic ordering and interactions, including potential local frustration. Reverse Monte Carlo modeling of the spin orientation demonstrated a relationship between the degree of cation inversion and the spin collinearity.

## OTHER APPLICATIONS

Kumar *et al.*<sup>13</sup> summarize recent studies and developments on the oxidation behavior of bulk HEAs and HEA coatings. The paper highlights the challenges and controversies for future research perspectives, particularly those on sustainability for different

applications. Based on available data of oxidation studies of HEAs, it is pointed out that transition metal-based HEAs have a better oxidation resistance than refractory-based HEAs and are also comparable with Ni-based superalloys. Apart from the elemental composition, the processing method, which controls microstructural evolution, is also identified as a significant factor affecting the oxidation resistance.

Torrento *et al.*<sup>14</sup> present a study on non-equiatomically TiNbZrTaMn and TiNbZrTaMo high entropy alloys for potential applications in biomedical technologies. The phase composition, microstructure, and selected mechanical properties were measured and compared with theoretical predictions. The elastic modulus of the samples remained above the theoretical predictions but lower than the commercial biomaterials. The Vickers microhardness values were higher than those of commercial biomaterials, indicating superior mechanical strength. The electrochemical corrosion tests indicated that the HEAs possessed superior corrosion strength. Altogether, the data indicate that TiNbZrTaMn depicts a better applicability potential for being used as a biomaterial in biomedical applications than some commercial materials.

Wang *et al.*<sup>15</sup> present a self-supported AlFeCoNiMo high entropy alloy with a uniformly distributed micropillar array structure on the surface. The catalyst exhibited an excellent oxygen evolution reaction (OER) catalytic performance, attributed to the unique micropillar array with rich active sites and the synergistic effect between multiple metallic elements. The good stability of the catalyst resulted from the steady micropillar array structure and the formation of oxyhydroxides on the surface during long-term catalysis. This work provides a facile and scalable method for the preparation of self-supported, low-cost, and high-performance oxygen evolution reaction electrocatalysts.

Kuo *et al.*<sup>16</sup> present a novel garnet-type high-entropy oxide as a solid electrolyte for Li-ion batteries,  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{0.4}\text{Ta}_{0.4}\text{Nb}_{0.4}\text{Y}_{0.6}\text{W}_{0.2}\text{O}_{12}$  (LLZTNYWO), which was successfully synthesized using a conventional solid-state method. Daily decay measurements revealed that LLZTNYWO exhibits the greatest air stability among all the doped samples tested, with no obvious decay in ionic conductivity. In addition, LLZTNYWO is found to have good electrochemical stability against lithium, making it a promising solid electrolyte for Li-ion batteries.

## DEFINING HIGH ENTROPY

In the literature, discrepancies exist between the nomenclature of “compositionally complex,” “high entropy,” and “entropy stabilized” materials. Brahlek *et al.*<sup>17</sup> provide a framework for classifying the differences between these terms, which is intended to bring a common language to this emerging area. This work highlights the critical importance of understanding the crystallinity, composition, and mixing length scales of these materials in determining a meaningful identification.

In conclusion, this special topic collection provides a valuable resource for the community interested in the latest developments in high-entropy materials and offers a comprehensive and up-to-date overview of the field's current state. We sincerely hope that readers of this special topic will find the collection of articles interesting and useful as a reference for future research in the emerging field of high-entropy materials.

## AUTHOR DECLARATIONS

### Author Contributions

**An-Chou Yeh:** Writing – original draft (equal); Writing – review & editing (equal). **Stéphane Gorsse:** Writing – original draft (equal); Writing – review & editing (equal). **Veerle Keppens:** Writing – original draft (equal); Writing – review & editing (equal). **Dustin A. Gilbert:** Writing – original draft (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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