This special issue puts into focus two unique classes of materials: High Entropy Alloys (HEAs) and Bulk Metallic Glasses (BMGs) that are increasingly applied as coatings via thermal spray, cold spray, laser cladding, or similar coating processes. The editorial team was excited to have received contributions from all over the globe and the 38 articles published in this issue relate to assessment, analysis, design implications, and challenges involving HEA
and BMG coatings. Collectively, this represents a vast body of current knowledge about the types of HEA and BMG coatings, and the influence of phase structure, microstructure, material properties and stability in the design and selection of HEA or BMG coatings for various applications.

The Taxonomy of High Entropy Alloys and Bulk Metallic Glasses Coatings

Members of this editorial team are fortunate for their positive engagements with Prof. S. Ranganathan, who published the seminal article: *Alloyed pleasures: Multimetallic cocktails* (Ref 1) in November 2003. In simple words, Prof. Ranganathan reminded the readers that they can mix more than two major elemental components together to form new classes of alloys. This shift from traditional binary or ternary phase diagrams to multicomponent alloys has led to the discovery and development of HEA and BMG materials.

**High Entropy Alloys (HEA):** First coined by one of our guest editors, Prof. Jien-Wei Yeh, HEAs have at least 5 major metallic elements \( n \geq 5 \), each having an atomic percentage between 5 and 35 at.% (Ref 2). There are four core effects: high entropy which enhances the formation of solution phases, severe lattice distortion from different atom sizes and chemical bonding, sluggish diffusion due to the distorted lattice, and the cocktail effect, which highlights HEA’s unique performance from synergistic element mixtures.

**Bulk Metallic Glasses (BMG):** These are a subset of amorphous metallic glasses that exhibit a non-crystalline structure and were first postulated by Prof. Akihisa Inoue (Ref 3) that mixing many metals \( n \geq 3 \) of different atomic sizes could achieve slow freezing rate to achieve BMGs. As the counterparts of HEAs, BMGs further require negative enthalpy of mixing and large atomic size differences of \( \geq 12\% \) between the alloying elements. Without any long-range order, most BMGs exhibit novel physical and chemical properties.

Therefore, over the past two decades, the material science community has focused on developing these multicomponent HEAs and BMGs for various industrial applications. However, given the monetary cost and availability of strategic metallic elements such as Zr, Co, Mo, and Ni, and technical challenges in large scale casting of chemically homogenous ingots, the use of HEA and BMG as feedstock for functional coating processes presents a viable and attractive technical solution. In this special issue, HEA feedstock containing CrFeCoNi base, as well as Fe-based BMGs remain as the dominant research interest.

**Perspectives on HEA and BMG Coating Research**

The use of HEAs and BMGs as functional coatings for various extreme engineering conditions and applications provides a positive outlook for commercial opportunity. Below are the editorial team’s perspectives on the future of surface engineering with HEA and BMG coatings.

1. As mentioned in an invited review on HEAs (Ref 4), the vast computational hyperspace offered by multi-principal element alloys requires high throughput techniques to predict useful compositions for exploration. During thermal spray and laser cladding coating processes, HEA and BMG feedstocks undergo rapid melting and solidification. Therefore, these thick HEA and BMG coatings often contain artefacts due to oxidation, phase changes, and inter-alloying (Ref 5). Researchers have to rapidly generate reliable data to build new relationships between these compositions, processing, coating microstructure, and properties. Integrated Computational Material Engineering (ICME) and solid solution ab Initio calculations tools will be as important as experimental x-ray diffraction data.

2. Cost factors and sustainability of HEA and BMG feedstocks are strong motivators for consideration when designing new alloys. For example, Ni/Co-free HEA or lightweight BMG coatings present significant opportunity for functional applications.

3. The key application areas of high temperature, tribology, corrosion, as well as niche areas like biomedical and electronic materials require specially tailored HEA or BMG coatings. These are areas where refractory HEAs, high entropy rare earth oxides, or BMGs with high entropy composition can be applied as coatings.

4. There is sufficient empirical evidence (Refs 5, 6), including from articles in this special issue, that multiphase HEAs within a coating can improve mechanical properties. This holistic view can be expanded to include oxide/carboide or carbide plus metallic HEA phases or multiple types of HEAs within a coating to broadly harness the “multi-metallic cocktail effect.”

Following from the above points and in the words of another HEA pioneer, Prof. B. Cantor (Ref 7): “The world of materials is massive and there are thousands of great things to discover.” Our current state of research, even in
the field of coatings, primarily involves four or five equiatomic HEAs that contain the CrFeCoNi base or Fe/Zr-based BMGs. Expanding this suite of materials to discover and create new non-equiatomic HEAs and other compositionally complex BMGs will motivate the field of research, resulting in the potential for coating systems that can be tailored for unique functional properties.

The editorial team has observed that collaboration research groups with similar interests and complementary expertise can exponentially accelerate HEA and BMG coatings research and development. Given the breadth of potential alloy compositions, as well as the wide range of thermal spray and laser cladding technology available, there is no need to “re-invent the wheel.” Research should focus on collaboration and generation of novel forms of HEA or BMG coatings for real world applications. The genesis of new HEA or BMG coatings is often through the sharing of ideas, for example, on studies pertaining to the impact of thermal spray processing conditions on final alloy composition. (Ref 6) While the Covid-19 global pandemic has disrupted face-to-face contact for many, we are hopeful that meetings such as the International Workshop on High Entropy Material (IWHEM) and International Symposium on Metastable, Amorphous and Nanostructured Materials (ISMANAM) will present opportune occasions for researchers, engineers, and scientists to re-emerge and proactively collaborate again.

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Dedication to Mentor It is timely and appropriate to recognize Prof. S. Ranganathan (Emeritus Professor & Senior Homi Bhabha Fellow, Indian Institute of Science, Bangalore, India), a pioneer in crystallography, quasicrystals, rapidly quenched materials, nanomaterials, and alloy design. The authors are grateful for his leadership and mentoring in physical metallurgy that has spanned 5 decades.

References

1. S. Ranganathan, Alloyed pleasures: multimetallic cocktails, Curr. Sci., 2003, 85(10), p 1404–1406.
2. J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau and S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, Adv. Eng. Mater., 2004, 6(5), p 299–303.
3. A. Inoue, Stabilization of metallic supercooled liquid and bulk amorphous alloys, Acta Mater., 2000, 48(1), p 279–306.
4. D.B. Miracle and O.N. Senkov, A critical review of high entropy alloys and related concepts, Acta Mater., 2017, 122, p 448–511.
5. A. Meghwal, A. Anupam, B.S. Murty, C.C. Berndt, R.S. Kottada and A.S.M. Ang, Thermal spray high-entropy alloy coatings: a review, J. Therm. Spray Technol., 2020, 29(5), p 857–893.
6. A. Anupam, R.S. Kottada, S. Kashyap, A. Meghwal, B.S. Murty, C.C. Berndt and A.S.M. Ang, Understanding the microstructural evolution of high entropy alloy coatings manufactured by atmospheric plasma spray processing, Appl. Surf. Sci., 2020, 505, p 144117.
7. B. Cantor, I.T.H. Chang, P. Knight, and A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. A, 2004, 375-377(1-2 SPEC. ISS.), p 213-218.

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