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High entropy alloys: Key issues under passionate debate

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ABSTRACT

The present Viewpoint set aims at providing a summary of the recent advancements in the fundamental understanding of high entropy alloys (HEAs) as well as igniting new ideas and activities in this rapidly evolving field of use-inspired basic research. The universality of the core effects in HEAs, ranging from configurational entropy contributions to cocktailing effects are still under a passionate debate and in particular the peer-reviewed articles are meant to provide original perspectives. The various contributions are strongly opinion-based in a variety of areas including diffusion, phase transformations, deformation behavior, corrosion, metastability, structural as well as functional properties. In addition, the impact of the original metallic HEAs onto the field of oxides and ceramics has been illustrated and the role of entropy in high-entropy oxides is critically discussed.

Strengthening of metallic materials by alloying has evolved from a trial-and-error to an innovative knowledge based endeavor. For a long time the adopted alloying strategy for single-phase metals involved a bottom-up approach, i.e. starting from a metallic matrix and adding secondary elements in small quantities to the primary base material. However, this approach restricts the possible number of combinations and hence, the alloys to be prepared. The need for a brand new alloying strategy, felt for some time, has finally emerged to provide novel materials with properties that can cope with stringent requirements to meet technological challenges.

Near the close of the 20th century and the beginning of the 21st century, one such a strategy based on “mixing together multi-principal elements” in high concentration to synthesize a new class of alloys was proposed by two stalwarts: Brian Cantor (in the early days affiliated with the University of Sussex, UK) and Jien-Wei Yeh (National Tsing Hua University, Taiwan) and collaborators. The history of the ‘nucleation and growth’ of the field of High-Entropy Alloys (HEAs) and of related concepts of Complex Concentrated Alloys (CCAs) looks like a ‘sluggish’ diffusional process itself.

Already in the1980s Brian Cantor suggested to research funding agencies in UK that it would be exciting to explore *multicomponent materials*, i.e. alloys made from equiatomic mixtures of many different components. Nevertheless the proposal was turned down with the unrelenting and inexorable phrase: ‘Please do something more sensible’. Indeed, it takes a pretty strong personality not to grasp the low hanging fruit as is usually done today but to address more principal ‘crazy’ questions in metallurgy, in materials science and materials engineering. That being said: along these lines Brian Cantor together with his young undergraduate student at Sussex, Alain Vincent discovered the fcc single-phase alloy with the composition $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ now well-known as the ‘Cantor alloy’ [1], see Fig. 1.

Much later in the 1990s ‘Cantor alloys’ were developed further, with additions of several other elements extending the manufacturing process to rapid solidification by melt spinning, at Oxford by Brian Cantor and collaborators (Peter Knight and Isaac Chang) [2]. Also another clever idea of the use of *equiatomic substitution* was explored (Ki-Buem Kim), i.e. to replace one or more of the components by an equiatomic mix of chemically similar components [3] in other than the ‘Cantor alloy’. For more details reference is made to [4].

Almost parallel over the same period of time a similar development on the novel design of alloys took place in Taiwan. In the mid 1990s, Jien-Wei Yeh developed independently the idea of alloys containing multiple principal elements in equal or near-equal proportions. Although most of his colleagues in Taiwan argued against the new alloy concept and anticipated that this will not work in the synthesis of any useful but rather brittle alloy, the National Science Council (now Ministry of Science and Technology) supported Jien-Wei Yeh to carry out the first 2-year integrated project

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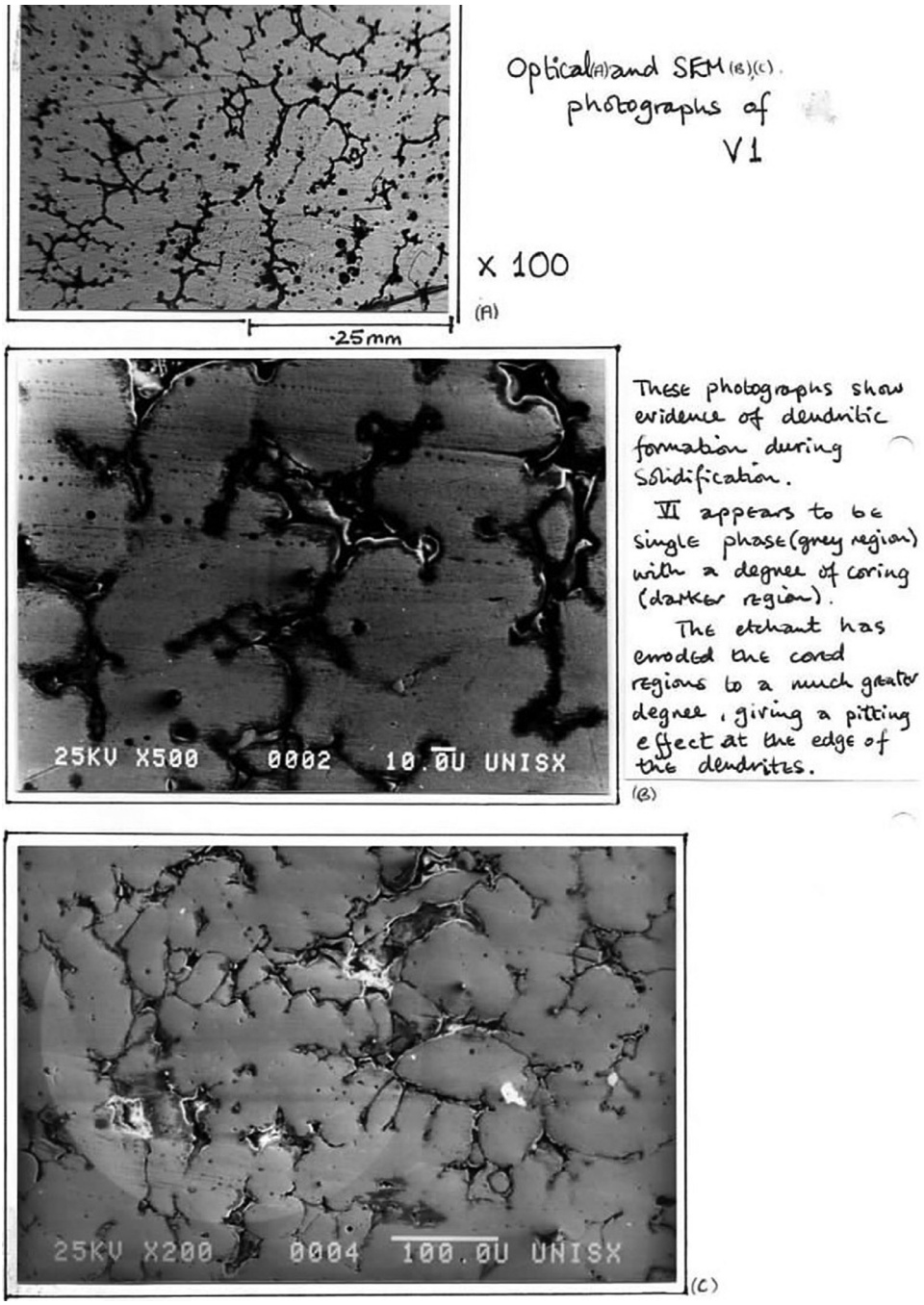

Fig. 1. The very first observations of a HEAs reported by undergrad Alain Vincent and supervisor Brian Cantor in BSc Thesis, University of Sussex,1981. Optical (top) micrograph and SEM images (middle, below) of dendritic formation in $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$, single phase (gray area) with a degree of coring (darker area). *Courtesy: Brian Cantor, at present University of Oxford and Brunel University London, Uxbridge, UK.*

on High-Entropy Alloys in 2001, which was based on the results of three earlier master's theses, the very first one in 1996 (see Fig. 2, [5]). After this successful exploratory period several faculty members and graduate students became engaged in various topics which contributed to establish a solid and sound base for HEAs internationally. Interestingly the same year as Brian Cantor [3], several papers were published in 2004, including the HEA concept paper in Advanced Engineering Materials [6].

A catchy new name, "High-Entropy Alloys (HEAs)" was coined by Yeh for any alloy containing at least 5 elements having concentrations varying from 5 to 35 atom%. As compared to the aforementioned traditional bottom-up approach, this sparkling idea involved the novel design of alloys by a rather top-down approach, in which no clear metallic matrix, some kind of a whole-solute-matrix, but only atoms exist in more or less 'defective' states. The subject of alloying has become a hot topic ever since this radical proposition, with theoretical as well as experimental developments on HEAs in general or complex concentrated alloys (CCAs) in particular. The popularity of HEAs in the literature has increased many folds in recent years and HEAs have taken a central stage in the field of modern materials science and engineering. The potential of HEAs/CCAs in various critical and demanding applications are beginning to be recognized and it is now evident that HEAs/CCAs are likely to remain as a central theme for both structural as

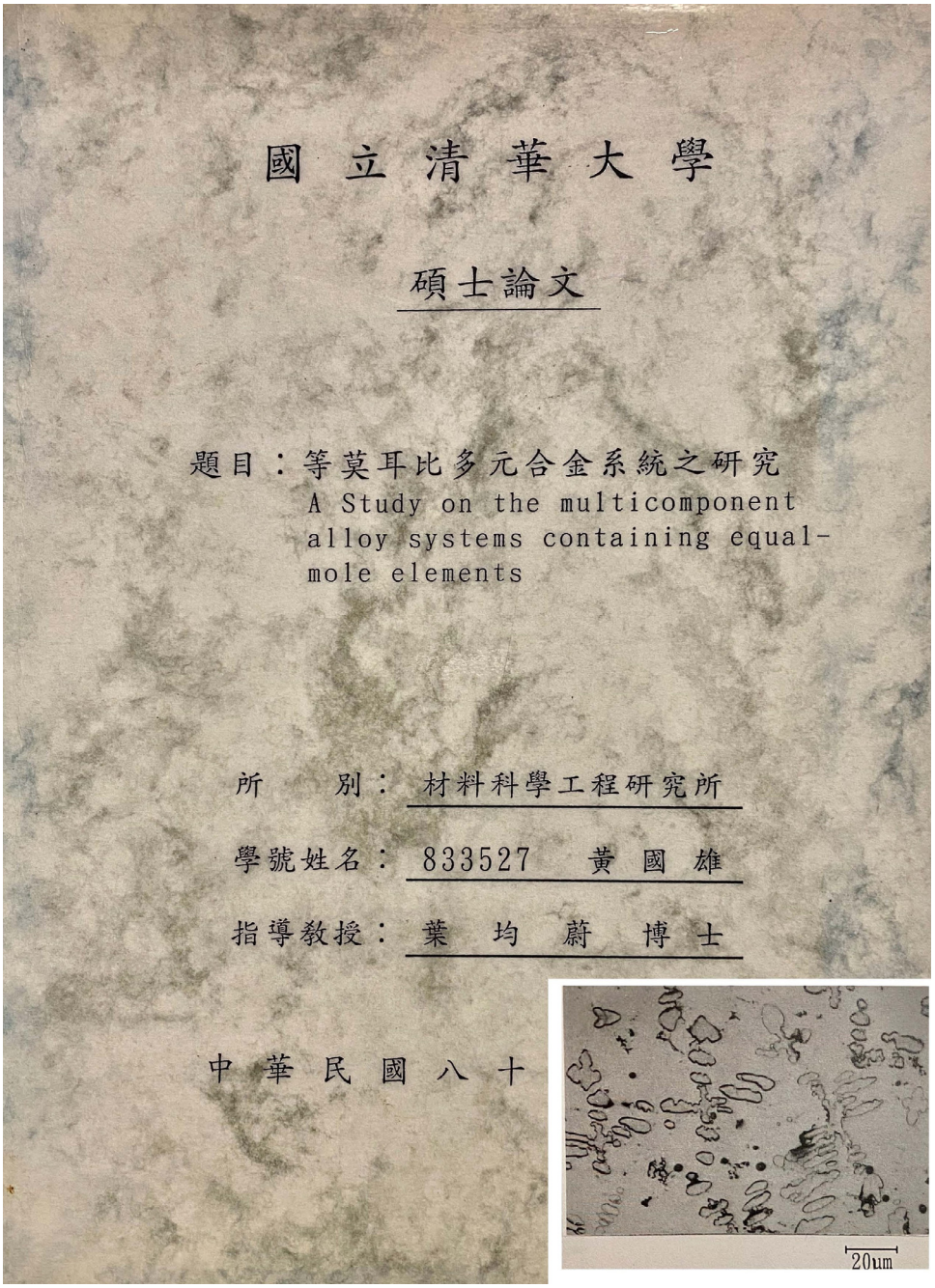

Fig. 2. The cover page of the very first MSc thesis on HEAs "A study on the multicomponent alloy systems containing equal-mole elements" carried out under the supervision of Jien-Wei Yeh at National Tsing Hua University, Taiwan, 1996. Insert: A typical dendritic cast of the microstructure of MoTiVFeNiZr showing multiple phases for equiatomic alloys synthesized by ingot casting route. *Courtesy: Jien-Wei Yeh, National Tsing Hua University, Taiwan.*

well as functional applications, at least for another decade or even longer.

Although the motivation of research activity on HEAs was primarily aimed at achieving simple solid solutions containing multiple components, which can easily be synthesized and used in practice, it has opened up many fundamental questions that need to be addressed. Recently, more attention is being increasingly paid to design and develop some "true" single phase solid solutions to probe and uncover fundamental mechanisms involving phase formation, thermodynamics, kinetics, diffusion, defects and properties. It should be realized that the theoretical feasibility of such a counterintuitive alloy design of HEAs stems from the concept of entropic stabilization, wherein large number of elements would raise the configurational entropy contribution of the solution state in lowering the Gibbs free energy.

In a sense, HEAs are the counterparts of (bulk) metallic glasses: the latter requiring a negative enthalpy of mixing favorable in certain processing routes from the melt and large differences in atomic sizes of the multiple elements so as to frustrate crystallization. For HEAs, it is just the opposite focusing on crystalline structures to generate materials over a wide spectrum of properties. For example, small differences in atomic sizes and no large differences in the enthalpies of mixing between unlike pairs are preferentially designed to favor crystalline solid solutions which are in general contributing to the requirement of ductility or toughness of single-phase materials.

Table 1
Overview VP set papers on HEAs with references to appropriate volumes and corresponding pages in Scripta Materialia.

Jae Wung Bae, Hyoung Seop Kim: *Towards ferrous medium-entropy alloys with low-cost and high performance*	Volume 186 September 2020 Pages 169–173 https://doi.org/10.1016/j.scriptamat.2020.05.030
Sebastian A. Kube, Jan Schroers: *Metastability in High Entropy Alloys: What can we learn from metallic glasses*	Volume 186 September 2020 Pages 392–400 https://doi.org/10.1016/j.scriptamat.2020.05.049
Abhishek Sarkar, Ben Breitung, Horst Hahn High: *Entropy oxides: The role of entropy, enthalpy and synergy*	Volume 187 October 2020 Pages 43–48 https://doi.org/10.1016/j.scriptamat.2020.05.019
Daniel Gaertner, Josua Kottke, Yury Chumlyakov, Fabian Hergemöller, Gerhard Wilde, Sergiy V.Divinski: *Tracer diffusion in single crystalline CoCrFeNi and CoCrFeMnNi high-entropy alloys: kinetic hints towards a low-temperature phase instability of the solid-solution?*	Volume 187 October 2020, Pages 57–62 https://doi.org/10.1016/j.scriptamat.2020.05.060
Weidong Li, Shuying Chen, Peter K. Liaw: *Discovery and design of fatigue-resistant high-entropy alloys*	Volume 187 October 2020, Pages 68–75 https://doi.org/10.1016/j.scriptamat.2020.05.047
Indranil Basu, Jeff Th. M. De Hosson: *Strengthening mechanisms in high entropy alloys: fundamental issues*	Volume 187 October 2020 Pages 148–156 https://doi.org/10.1016/j.scriptamat.2020.06.019
Yung-Ta Chen, Yao-Jen Chang, Hideyuki Murakami, Stéphane Gorsse, An-Chou Yeh: *Designing high entropy superalloys for elevated temperature application*	Volume 187 October 2020 Pages 177–182 https://doi.org/10.1016/j.scriptamat.2020.06.002
Xuehui Yan, Yong Zhang: *Functional properties and promising applications of high entropy alloys*	Volume 187 October 2020 Pages 188–193 https://doi.org/10.1016/j.scriptamat.2020.06.017
Yiping Lu, Yong Dong, Hui Jiang, Zhijun Wang, Zhiqiang Cao, Sheng Guo, Tongmin Wang, Tingju Li, Peter K. Liaw: *Promising properties and future trend of eutectic high entropy alloys*	Volume 187 October 2020 Pages 202–209 https://doi.org/10.1016/j.scriptamat.2020.06.022
William A Curtin, Wolfram Georg Nöhring: *Design using randomness: a new dimension for metallurgy*	Volume 187 October 2020 Pages 210–215 https://doi.org/10.1016/j.scriptamat.2020.06.012
B. X. Cao, C. Wang, T. Yang, C. T. Liu: *Cocktail effects in understanding the stability and properties of face-centered-cubic high-entropy alloys at ambient and cryogenic temperatures*	Volume 187 October 2020 Pages 250–255 https://doi.org/10.1016/j.scriptamat.2020.06.008
Lewis R Owen, Nicholas Gwilym Jones: *Quantifying local distortions in alloys*	Volume 187 October 2020 Pages 428-433 https://doi.org/10.1016/j.scriptamat.2020.06.030
Daniel B. Miracle, Ming-Hung Tsai, Oleg N. Senkov, Vishal Soni, Rajarshi Banerjee: *Refractory high entropy superalloys (RSAs)*	Volume 187 October 2020 445–452 https://doi.org/10.1016/j.scriptamat.2020.06.048
K. Guruvidyathri, M. Vaidya, B. S. Murty: *Challenges in Design and Development of High Entropy Alloys: A Thermodynamic and Kinetic Perspective*	Volume 188 November 2020 Pages 37-43 https://doi.org/10.1016/j.scriptamat.2020.06.060
Jian-Hong Li, Ming-Hung Tsai: *Theories for predicting simple solid solution high-entropy alloys: classification, accuracy, and important factors impacting accuracy*	Volume 188 November 2020, Pages 80-87 https://doi.org/10.1016/j.scriptamat.2020.06.064
John R. Scully, Samuel B. Inman, Angela Y. Gerard, Christopher Taylor, Wolfgang Windl, Daniel K. Schreiber, Pin Lu, James E. Saal, Gerald S. Frankel: *Controlling the Corrosion Resistance of Multi-Principal Element Alloys*	Volume 188 November 2020 Pages 96-101 https://doi.org/10.1016/j.scriptamat.2020.06.065

Owing to its inherent complexity, multi-component HEAs/CCAs have been observed to display peculiar characteristics that were summarized by Yeh and co-workers as the four core effects viz. i) high entropy mainly due to configurational entropy; ii) lattice distortion due to large variation in atomic sizes of constituent elements and mutual chemical bonds; iii) sluggish diffusion kinetics due to lattice distortions and iv) overall properties due to diverse multi-level microstructure, also referred to as the "cocktail" effect. The present key issues are the following:

- The universality of these core effects in HEAs is still under a passionate debate, in particular, issues related to 'sluggish diffusion' and the 'cocktailing effects'. The latter was first proposed by Srinivasa Ranganathan in 2003 [7], in fact not a 'novel core' effect but rather a reminder and a warning that as far as properties of HEAs/CCAs are concerned a simple linear superposition of the properties of individual components is not going to work. Also the original idea of the entropic stabilization of solid solutions needs to be assessed for different systems since mixing enthalpies due to chemical bonding and lattice strain are equally important competing factors and may even outweigh the entropic contributions at room or relatively low temperature. High temperature is definitely an important factor for entropy stabilization of solid solution phases and without an entropy of mixing rather intermetallic compounds can be formed.

  Therefore, the broader picture can be summarized as follows: In addition to those composition regions in which a single phase is stable, the majority of the alloy compositions yield multiple phases during solidification or decompose to more than one phase upon long annealing treatment. As a consequence, further studies with improved and experimentally validated isothermal TTT (transformation-time-temperature) diagrams should be carried out to manifest the effect of temperature and time on phase transformations at various time and length scales.

- Another key issue is related to the fact that the classical definition of defects and their impact on structure-property relationships does not seem to be applicable for high entropy alloys. This is so because the 'reference state' is not a perfect matrix in which well-defined point, line, and planar defects are embedded. For a whole-solute matrix, we have to deal with fluctuations and local deviation of 'defects in a defective reference state'. To highlight a few remarkable consequences: moving and stationary dislocations will never be very straight on various time and length scales; second, even a Burgers vector is less well-defined due to the non-translational invariant reference lattice and third, grain-boundaries could be strengthened by chemical and geometrical lattice distortions and as a consequence the transmittance of dislocations as well as grain-growth at relatively high temperatures might be substantially suppressed. This 'defective reference state' will also have serious consequences on the diffusion behavior in these multi-component alloys. In general, we may state that the research done so far clearly indicates that the traditional materials science concepts of 'defects in solids' cannot directly be extended explaining some of the newly observed phenomena.

Aim of the VP set: Right from the onset of HEAs/CCAs, it has been realized that the fundamental understanding is critical to guide design of alloys for improved performance and potential applications in various high-end applications. HEAs as complex solid solutions, in fact, are most crucial from the basic scientific view point because of the fact that the conceptual advances are indeed

necessary to bridge the gap between well studied and understood dilute solid solutions and poorly understood concentrated solid solutions. To take stock of the advancement in the area of HEAs/CCAs in the last one and half decades, the present VP set is envisaged to provide the researchers actively involved in this rapidly advancing field the state of the art as well as key questions that need to be addressed. Unlike several special issues in the literature, this VP set is deemed to be distinct as fundamental issues pertaining to design, microstructure-evolution and stability, properties, and microstructure-property correlation of HEAs are addressed.

Since many excellent reviews are available already (for a couple of recent ones see e.g. [8–11]), this VP set cannot be regarded as a collection of review articles. On the other hand, the articles in the VP set are meant to provide original perspectives and are strongly opinion-based in a variety of areas including diffusion, phase formations, deformation behavior, solid solution hardening, lattice distortion, metastability, structural and also functional properties, possible applications, et cetera. In addition, the impact of the original ideas of the metallic materials onto the field of oxides and ceramics has been illustrated in this VP set. In particular, the role of entropy, enthalpy, and synergy arising from the presence of multiple elements in high-entropy oxides are presented and critically discussed.

Interestingly with a palette of a large number of elements in the periodic table, almost unlimited combinations can be explored. Hence, machine learning based approaches become important to effectively design and develop futuristic materials, required to meet the stringent requirements of many demanding applications. In contrast to 'high throughput experimentation', the machine learning approach could be more rewarding. Nonetheless, experimental and theoretical explorations will remain key for serendipitous discovery of novel alloys, as evidently was done by Brian Cantor and Jien-Wei Yeh for HEAs/CCAs. We strongly believe that this VP set will provide an excellent summary of the recent advancements in the fundamental understanding of HEAs, as well as ignite new ideas and activities in this fascinating and rapidly evolving field of use-inspired basic research.

Table 1.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2020.07.010.

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