

## High entropy materials\*

High entropy materials (HEMs) are considered to be a new 'avatar' in physical metallurgy and materials engineering. After their seminal discovery in 2004 (refs 1, 2), research activity in HEMs and related materials has been vigorous for the last 13 years. In recent times, HEMs have gained tremendous attention due to their attractive and adjustable properties with a large compositional range and fascinating microstructures. Although the initial discovery was on high entropy alloys (HEAs) consisting of different metals, the research areas have been expanded to different classes of materials such as high entropy refractory alloys, high entropy superalloys, high entropy metallic glass and high entropy ceramics (oxides/nitrides/carbides). Therefore, these are now termed as HEMs.

Traditionally, alloy design strategy involves alloys based on one or two components. However, HEAs are multicomponent solid solutions containing at least five elements or compounds with equimolar or near equimolar composition<sup>1-3</sup>. This multimaterial combination was named as 'multimetallic cocktails' by Ranganathan<sup>4</sup> prior to its discovery in 2003. Thus, it has become an exciting research area in materials science. It has also added a new dimension to physical metallurgy and materials science indicating an apparent paradigm shift in the strategy of materials design, and opened up new vistas of the design and development of materials.

It started with the opening remarks by President and former president of NTHU, Y. M. Peng (President of Materials Research Society of Taiwan (MRS-T)), J.-W. Yeh (NTHU), B. Cantor (University of Bradford, UK), P. K. Liaw (University of Tennessee, USA), O. N. Senkov (Air Force Research Lab, USA) and S. Ranganathan (Indian Institute of Science, Bengaluru).

The technical session began with a plenary lecture by C. T. Liu (City University of Hong Kong) on the strengthening of HEAs using hard intermetallic phases. He showed that it was possible to strengthen HEAs with face centred cubic (FCC) structure by precipitating the complex intermetallic phase, including brittle  $\sigma$  and  $\mu$  phases. This was followed by four keynote lectures. Daniel Miracle (Air Force Research Lab, USA) provided a critical review of the HEMs and related concepts. He suggested developing high-throughput experiments as well as computation for detailed structural analysis. R. Ritchie (U.C. Berkley, USA) demonstrated the promising mechanical properties of CrCoNi-based HEAs. With exceptionally high fracture toughness ( $K_{IC} \sim 217 \text{ MPa m}^{0.5}$  at 77 K), he demonstrated that these materials exhibit mechanical behaviour similar to low stacking fault materials, such as stainless steel. C. Koch (North Carolina State University, USA) described how to prepare low-density (3–5 g/cc) HEMs ( $\text{Al}_{20}\text{Li}_{20}\text{Mg}_{10}\text{Sc}_{20}\text{Ti}_{30}$ ) by proper selection of alloying elements and processing techniques, mechanical alloying followed by spark plasma sintering. E. George (University of Bochum, Germany) discussed the phase stability and mechanical behaviour of the first HEM, CrMnFeCoNi, which is also known as Cantor alloy after the name of its discoverer. He showed that at least some of the single-phase HEMs were metastable in nature and decomposed into many intermetallic phases during slow cooling from high temperature.

In the conference, 106 contributed papers and 57 posters were presented during the next one and half days. Apart from physical metallurgy and phase formation, few areas in which research work was presented are worth mentioning. These are mechanical behaviour, high-temperature properties, and solid state physics related to HEMs. U. Glatzel (Germany) in his invited lecture introduced the new German Priority Programme on compositionally complex alloys, including HEMs. S. Ranganathan delivered an invited lecture on the application of Pettifor map, a powerful tool to explain the formation and prediction of HEAs. He mentioned that it may be possible that the 'cocktail effect' can lead to

extended solid solution beyond the classical factors (size, electronegativity and valence electron concentration).

B. S. Murty (IIT Madras) described the future challenges in understanding phase formation and microstructural evolution in HEAs. R. Banerjee (University of North Texas, USA) presented recent work about using the combinatorial approach on  $\text{Al}_x\text{CrCuFeNi}_2$  complex concentrated alloys prepared by laser-engineered net-shaping process, leading to the development of compositionally and microstructurally gradient structure. O. Senkov (Air Force Research Lab, USA) made a presentation on the development of HEMs using refractory metals (Nb, Mo, Hf, Ta, W, Re, etc.) with both computational and experimental approaches. H. J. Ryu (Korean Advanced Institute of Science and Technology, Korea) described the work done on powder metallurgy of refractory HEAs. P. Liaw discussed the different possibilities of deviation from equilibrium configuration and described the concepts with interesting examples. P. P. Bhattacharya (IIT Hyderabad) delivered an invited talk on texture evolution in the deformed and annealed CoCrFeMnNi alloy, and showed that evolution of the texture in the deformed material is a typical characteristic of low-stacking-fault materials. Y. Lu (Dalian University of Technology, China) provided a glimpse of eutectic HEMs, a novel design concept. By achieving unique microstructure consisting of alternating soft and hard FCC phases, the bottleneck of low ductility can be apparently taken care of.

A substantially large number of papers were presented on different mechanical properties of HEAs, including fatigue, fracture and damage tolerance at room temperature, cryogenic and elevated temperatures. M. A. Meyers (UC Davies, USA) and R. Misra (University of North Texas) discussed work on mechanical behaviour in terms of shear localizations, slip trace analysis as well as usage of strain rate jump tests to understand the micromechanics of deformation in HEAs. I. Baker (Dartmouth College, UK) described the novel strategy of utilizing interstitial strengthening in HEAs, different from classical substitutional solid solution. K. R. Lim (Korea Institute of Materials Science) and E. Ghassemali

\*A report on the first International Conference on High-Entropy Materials (ICHEM) held at the National Tsing Hua University from 6 to 9 November 2016 at the University. It was organized by J.-W. Yeh, one of the discoverers of HEM. It was attended by more than 200 delegates from 21 countries. The conference website provides a detailed programme and themes (<http://ichem2016.conf.tw/site/page.aspx?pid=901&sid=1094&lang=en>)

(Jönköping University, Småland, Sweden) presented comprehensive work on the fracture of dual-phase HEAs, a starting point to understand the effect of the second phase of mechanical response of HEAs. The effect of soft FCC solid solution phase on the propagation of a crack in a dual-phase HEA was shown to be substantially reduced by the presence of the softer phase. R. S. Kottada (IIT Madras) provided a detailed analysis of creep behaviour of CoCrFeNi HEA by carrying out constant stress compression creep experiments on sintered nanocrystalline CoCrFeNi alloy.

There were also a large number of papers on the use of computational methods to understand phase formation, selection of HEMs in metallic and ceramic systems. M. Widom (CMU, USA) discussed the first-principle determination of entropy, a vital aspect in the design and selection of HEMs. T. Egami (University of Tennessee, USA) and Y. Yang (City University of Hong Kong) showcased techniques to measure atomic stress in the complicated HEA lattice. Using ab-initio calculations, they have shown that a large internal stress (~50 GPa) can be created due to charge transfer among the constituent elements in HEMs. A. Takeuchi (Tohoku University, Japan) discussed future prospects of HEAs with the hexagonal structure using a statistical scheme. Meha Bhogra (JNCASR, Bengaluru) made a presentation on the use of first-principle study on the stability of phases in different HEAs. There were two sessions devoted to modelling using CALPHAD approach. F. Zhang (CompuTherm, USA) and H.-L. Chen (Thermo-Calc, Sweden) gave a presentation on the role of these approaches in the design and development of novel HEM-forming compositions. K. Biswas (IIT Kanpur) provided a comprehensive study on the use of CALPHAD approach to predict both FCC and BCC single-phase HEAs. Simultaneously, K. Biswas *et al.* used experiments to corroborate and confirm the theoretical predictions, which show a reasonably good match. K. Guruvidyathri (IIT Madras) presented work on theory and experiments in the prediction of phase in AlCoCrMnNi HEA. L. Vitos (KTH, Sweden) delivered an invited lecture on the use of ab-initio alloy theory to study magnetic and mechanical properties, especially plastic deformation of HEAs. J. Dolinsek (Jozef Stefan Institute, Slovenia) discussed magnetism in rare-earth

Ho-Dy-Y-Gd-Tb hexagonal HEA. According to him, these novel categories of HEAs exhibited rich and complex magnetic field-temperature diagrams. The hydrogen storage property of CrFeMnTiVZr HEAs was presented by P.-H. Lee (NTHU). Y. Wu (University Science and Technology, China) showed the giant magnetocaloric effect in rare-earth HEAs. T. Nagase (Osaka University, Japan) delivered a lecture on the effect of irradiation on solid-state amorphization in HEAs by *in situ* observation using a high-voltage electron microscope. Shape memory effect in HEAs was discussed in detail by Y. Huang (University of Sheffield). Wear resistance of HEAs and development of novel HEAs for wear-resistant applications were discussed in detail by M. G. Poletti (Torino University, Italy).

The use of novel processing techniques to develop different applications of HEMs is important. A. Anupam (IIT Madras) presented work on nanomechanical properties of plasma-sprayed HEMs for coating applications. The use of powder metallurgical routes to prepare bulk HEAs was discussed by Y. Liu (Central South University, Hong Kong) and Rahul Mane (IIT Hyderabad). Preparation and characterization of NiCrMnY HEA thin-film resistors were discussed by Y.-C. Lee (National Pingtung University of Science and Technology, China). The use of gas atomization to prepare AlCoCrCuFENiSi powder for additive manufacturing was shown by C.-C. Yang (Industrial Research Institute of China). M. Kramer (Ames Lab/Iowa State University, USA) made a presentation on alloy optimization in terms of alloying elements and their composition for high-temperature applications. He mentioned that processing of HEAs would play a critical role in obtaining the desired microstructure and phases for high-temperature applications. S. Mileiko (Institute of Solid State Physics of RAS, Russia) delivered an invited lecture on high HEA-based metal matrix composites for high-temperature applications. These HEA composites contain different oxides, such as ZrO<sub>2</sub> and YAG to improve the high-temperature properties. K.-C. Lo (NTHU) discussed the development of oxidation-resistant (up to 1400°C) refractory HEAs for high-temperature applications. There were also a few papers on high-entropy glasses. L. Kandanswamy (Anna University, Chennai) presented detailed re-

search work on the fabrication of HEA composites with an assessment of mechanical properties in correlation to the microstructural investigation. Y. Pan (Southeast University, China) discussed the nanoscale property measurements of Cu-rich HEA metallic glass.

K.-C. Chang (NTHU) presented a poster on the development of HEA binder for selective laser melting to fabricate hard metal applications including tungsten carbide. The single-crystal growth of Al<sub>0.3</sub>CoCrFeNi was presented by Q. Xing (Ames Lab). Single crystals of ~6 mm diameter and ~25 mm length were prepared by the Bridgman method. Microwave processing of FeCoNiCrAl and FeCoNiCrCu HEA was presented by E. Colombini (University of Modena, Italy). The thermal stability of (Cr, Mo, Nb, Ru, Ta, V) HEA as diffusion barrier in Cu alloy thin films was studied by Y.-S. Hsiao (NTHU). The phase transformation in FeCoCr(Si, Ti, Mo, Nb, W) HEA coating fabricated by laser cladding was presented by Y. Guo (Guizhou University, China). With a proper selection of laser parameters, a sound coating could be formed. C. R. Wang (Tunghai University, Taiwan) presented work on the superconducting behaviour of TiVNbMoTa HEA with  $T_c \sim 4$  K. Interestingly,  $T_c$  could be changed by changing local composition. Although no theoretical explanations were provided, this work showed superconducting behaviour of HEMs.

Overall, the first international conference on HEMs showcased the intense research activities encompassing processing and properties of novel HEAs, the use of novel characterization techniques to study the mechanical, physical and functional properties of HEAs, phase formation, stability and various applications.

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