MEETING REPORT

High entropy alloys: a renaissance in physical metallurgy*

Physical metallurgy deals with the various issues of metallic alloys pertaining to composition and processing routes leading to evolution of phases with a variety of structures and microstructures with resultant properties with an aim to design and develop metallic alloys useful for technological applications. In 1926, solid solution of metallic elements in a crystalline framework, which was conceived as one of the important steps for successful alloy design, was proposed by William Hume-Rothery considering the size, electronegativity, valence electrons and crystal structure of the individual metallic elements, restricted to binary alloys. It is anticipated that the intermetallics or composites of immiscible elements can form if they do not conform to the Hume-Rothery rules for solid solution. However, after the discovery of concentrated solid solution alloys, there is a need to understand the principles behind the solid solution of multicomponent alloys containing five or more elements in high concentration. Thus the concept of high entropy alloy (HEA) was advocated by Yeh *et al.*[1] in 2004, while interpreting the stabilization of these multicomponent equiatomic or near-equiatomic disordered solid solutions in metallic alloys. The multimetallic combination of metals was termed 'multimetallic cocktails' by Ranganathan[2] in 2003 and became the first journal publication heralding this new field of alloys. Now, for multicomponent concentrated alloys the formal definition of this special class of materials (HEAs) has been put forward as the alloy containing five or more elements with concentration ranging from 5% to 35%, leading to a simple disordered solid solution structure. The interested researchers are referred to the recent book published by Murty *et al.*[3] reviewing all aspects of the work reported on HEAs. It is a matter of pride for us that this first book on the new realm of research is authored by two Indians and a Taiwanese. There is now a lot of excitement and new activities, as it has opened up several fronts for discovering newer alloy systems for demanding technologies. In a way it has ushered in 'A renaissance in physical metallurgy'.

Keeping in view the current excitement and interesting activities in this area, a workshop on HEAs in India was organized recently. K. C. Harikumar (IIT Madras, Chennai) and Bala K. Bharadvaj (Boeing India) welcomed the delegates and briefly mentioned the importance of the present workshop in the context of materials development. B. S. Murty (IIT Madras) introduced the theme and highlighted how the idea had originated to organize such a scientific meeting. S. Ranganathan (IISc, Bengaluru) in his presidential remarks highlighted the multicomponent alloys in the context of bulk metallic glasses and HEAs. He emphasized the importance of cocktail effects in multimetallic alloys. It is pertinent to point out that Brain Cantor (UK) shared his views on HEAs through a video message during the inaugural session, where he pointed out his initial work on multicomponent alloys is similar to HEAs since 1980, which was published[4] in 2004. There were nearly 100 participants (mainly from metallurgy and materials science fraternity) from various institutions such as IITs, NITs, JNCASR and IISc, and organizations like DMRL, NMRL, ARCI, IGCAR, BARC, ISRO, Boeing and GE as well as four speakers from abroad. There were 24 invited talks by experts and 21 poster presentations mostly by young researchers and students. It is interesting to note that there were two special discussion sessions devoted for brain storming based on the issues presented in the various sessions. The aim of the workshop was to bring the scientists and experts to exchange views and discuss matters ranging from theoretical modelling and simulation, thermodynamics, synthesis, processing, characterization, property evaluation and possible applications. In the following sections some of the interesting ideas which have emerged from the workshop are highlighted.

In his inaugural address, J. W. Yeh (NTHU, Taiwan) discussed the various aspects of physical metallurgy in the context of HEAs. His group has been persistently working in this area of multicomponent alloys since 1995 and had put forward the idea of HEAs in 2004. It was brought out that the high entropy arising due to randomness in the configuration of atoms is attributed to stabilizing the phases. However, in addition to high entropy three other core effects such as sluggish diffusion, lattice distortion and cocktail effects were also highlighted. Ranganathan pointed out the limits and extensions of solid solutions while discussing the Hume-Rothery principles. He also pointed out the importance of the bond factor proposed by David Pettifor in 1984, where Mendeleev number was assigned to each element and Pettifor maps were constructed, which has been extended to explain the formation for intermetallics as well as for quasicrystals and metallic glasses. He attributed cocktail effects in the multicomponent system to the extension of solid solution. D. B. Miracle (Air Force Research Lab, USA) delivered a talk on accelerated discovery and development of multi-principal element alloys (MPEs) via Integrated Computational Materials Engineering (ICME). He demonstrated that a palette of 40 metallic elements offers the possibility of 10^{10} MPEs and hence new methods are required to design and evaluate alloy systems quickly, systematically and effectively. A three-stage approach was discussed involving Calculation of Phase Diagram (CALPHAD) methods integrated with experiments on materials libraries with controlled composition and microstructure gradients with reference to aerospace alloys. Rajiv Mishra (North Texas, USA) dealt with the fundamental deformation science in the context of highly concentrated solid solution alloys such as HEAs, involving three distinct factors encompassing strain rate dependence, role of nanotwinning and grain size dependence. He mentioned that there is a possibility of attaining exceptional mechanical properties in this kind of alloy system as it is different from the dilute alloy systems containing single principled element.

Murty discussed the excitement and challenges in the field of HEAs. He

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pointed out that there is a real challenge for predicting the evolution and stability of these phases in the multicomponent system in a given processing condition. It has been shown that there are examples where the intermetallic phases and phase separation have been observed. He also emphasized that the formation of nanocrystalline HEAs has made them more interesting due to their fundamental and technological importance. Chris Berndt (Swinburne University, Australia) presented his work on thermal spray routes for achieving HEA structure on the surface of the substrate. Nanostructured AlCoCrFeNi and MnCoCrFeNi HEAs were preapared by ball milling followed by plasma-spraying. Then the mechanical properties of two HEA coatings were characterized and compared to plasma-sprayed NiCrAlY bond coats for the purpose of developing an alternate bond-coat material for thermal barrier coating system. Hari Kumar brought out the real challenges in thermodynamic modelling of multicomponent systems. He mentioned that CALPHAD provides a framework for computing phase stability-related multicomponent alloys utilizing the Gibbs energy databases and the computational thermodynamic tools. Anandh Subramaniam (IIT Kanpur) discussed orientational HEAs and brought out the importance of orientational entropy in the cluster compounds in the context of HEAs. He demonstrated in $GaMo_4S_8$ that at temperatures greater than 50 K, the entropic benefit is dominant to stabilize the disordered solid solution phase in preference to the orientationally ordered lower symmetry compound. S. R. Bakshi (IIT Madras) presented microstructures and mechanical properties of multicomponent NiTiCuFe multicomponent alloys. The as-cast structure showed a mixture of BCC and FCC phases. However, after thermomechanical processing, three phases such as Cu–Ni FCC, Fe_2Ti Laves phase and Ni_3Ti intermetallics were observed. The mechanical properties, corrosion and oxidation properties were found to be comparable to those of stainless steel. P. P. Bhattacharjee (IIT Hyderabad) studied the microstructure and texture evolution in the thermomechanically processed FCC CoCrFeMnNi HEA. It is interesting to note that deformation texture of the heavily cold-rolled HEA exhibits the strong brass component, a signature of typical low stacking fault energy materials. After subsequent annealing at low temperature, a fine microstructure along with α-fibre and recrystallized texture was observed. The observed microstructural and textural changes suggest the unique behaviour of HEAs compared to the low stacking fault energy alloys.

R. Krishnan (ex-BARC and DRDO, Bengaluru) elaborated the selection principles for possible HEAs in three areas – advanced ultra super critical (AUSC) coal-powered station, radiation environment, and aero-gas turbine engines. Evaluating the data, it was proposed that for AUSCs the following components can be investigated: (i) oxide dispersion strengthened low stacking fault energy FCC alloys such as FeCrCoMnNi with Y_2O_3 dispersions; (ii) high-strength Fe-$CoCrNi_2Al$ alloy with minor additions of Mo, Ti, or Si, either singly or in combination and (iii) FCC HEA matrix with B2 dispersions such as $AlCoNiFeTi_{0.4}$ and $Al_{0.3}CoCrfeNi$. For radiation environment with reference to fast breeder reactor fuel clad a combination of Fe-AlCrMoSiTi, not necessarily in equal atomic proportions, such that it leads to a low SFE BCC alloy with adequate ductility and strength should be studied. For high-pressure gas turbine rotors, a multiphase HEA from NbFeAlCrTiNiMo as well as MoNbTaVW may be worth considering. While designing the suitable alloys, it is suggested that HEAs should be taken as base and then make minor additions to get the desired microstructure and mechanical properties. J. D. Cotton (Boeing, USA) reviewed the Boeing work evaluating potential for low-density airframe alloys, as well as combinatorics-based model for predicting complex alloy behaviour in which 600,000 possible equiatomic compositions containing up to six components were evaluated. It has also raised the question of the effective ability of configurational entropy to extend the useful solid solubility range of the disordered phases. K. G. Pradip (RWTH Aachen, Germany) discussed the importance of single-phase solid-solution HEAs following the non-equiatomic HEA design. In some selected systems, it has been shown that these new classes of non-equiatomic multicomponent alloys can lead to outstanding properties arising out of pure solid solution strengthening. The use of quantum mechanically guided high throughput technology has been suggested for synthesis of non-equiatomic HEAs. Joysurya Basu (IGCAR, Kalpakkam) highlighted the importance of high-resolution analytical electron microscopic studies to understand the phase evolution and their distribution in nanoscale so as to understand the underlying mechanisms for their evolution. He has studied the precipitation of carbide phases and their conversion to oxycarbides at later stages in FeCoNiCr alloys using STEM-EELs technique. R. Koteswara Rao (UoH, Hyderabad) studied structure, phase stability and mechanical properties of microcrystalline and nanocrystalline Ti-Ni-Cr-Co-Fe HEAs. Alloys were prepared by ball milling and then sintered by spark plasma sintering (SPS) at 0.5 T_m and 0.6 T_m. The results of both micro and nanocrystalline HEAs seem to be encouraging for potential applications. S. Abhaya (IGCAR, Kalpakkam) studied the defects in HEAs using positron annihilation spectroscopy technique. It has been shown that this technique is useful to understand the defect recovery and crystallization in arc melted FeCrCoNi alloy using positron lifetime and implantation-induced defect evolution and defect annealing in 1.5 MeV Ni implanted for two doses using variable low energy positron beam. Ravi Sankar Kottada (IIT Madras) reported thermal stability and mechanical behaviour of CoCrFeNi HEAs, developed by mechanical alloying and spark plasma sintering. It has been shown that thermal stability of the microstructure in the range of 700–900°C for a duration more than 500 h is excellent. Room temperature and high-temperature mechanical properties of these alloys exhibited promisingly high compressive strength and plastic strain. Vinod Kumar (NIT, Jaipur) dealt with synthesis and characterization of light-weight AlMgFeCuCr-Ni HEAs, where two phases (BCC and FCC) were observed. Effect of sintering of the ball-milled powders was studied. Krishanu Biswas (IIT Kanpur) elaborated the pertinent issues on processing and stability of HEAs. The approach of ICME to select the elements and their composition in order to obtain single phase has been adopted. It has been shown that novel sinter-ageing techniques are beneficial in order to retain the nanocrystalline grains for better stability at high temperatures. K. Sivaprasad (NIT, Tiruchirapalli) studied CNT (carbon nanotube) reinforced nanocrystalline AlCrCuFeNiZn HEA composites. The sintered alloys exhibited phase separation of BCC to two FCC phases and hardness around 6.3 GPa. From the indentation fracture studies, it was demonstrated that CNTs as reinforcement phase can enhance fracture toughness even in brittle HEA materials. G. Phani Kumar (IIT Madras) discussed the challenges in extending the interface response function concept in the solidification of multicomponent alloys. This approach involves different physical properties that are required for the calculation, verification of the validity of the underlying assumption in the theory and a set of controlled experimental studies. R. Sankarasubramanian (DMRL, Hyderabad) elaborated on the issue that integrating microstructural modelling and simulation with experiments has become an essential part of the developments of new materials. It was pointed out that density functional theory (DFT)-based first principles calculations, molecular dynamics and Monte Carlo simulations are widely used atomic modelling techniques. Some of the key challenges in the atomistic modelling of multicomponent alloys were discussed and possible solutions are highlighted. Abhik Chowdhury (IISc, Bengaluru) presented phase field modelling approach for microstructural evolution in multi-phase multicomponent alloys, thus highlighting the utility of the phase field method both in the context of ICME as well as modelling of microstructures in HEAs. Jatin Bhatt (VNIT, Nagpur) utilized thermodynamic modelling for predicting metallic glass formation in HEAs. P_{HSS} parameter analogous to glass formability has been used to distinctly categorize solid solution forming HEAs from metallic glass (MG) forming alloys. The capability of the P_{HSS} model and the scope for further research in the direction of HEAs were discussed.

From the various discussions and analyses mainly during the two brainstorming sessions chaired by Atul Chokshi (IISc, Bengaluru) and Hari Kumar respectively, and 'The way-forward' session chaired by Ranganathan, several important points on this fascinating area have emerged with much clarity. In fact, it has now become clear that the alloy-design strategy of combining multiple elements in near-equiatomic proportions has tremendous potential for developing novel materials under the category of HEAs. However, there are several unresolved matters related to elemental distribution, exact calculation of phase selection, phase stability at lower temperature, exact contribution and measurement of configurational entropy, phase separation, role of misfit strain and its estimation at the level of nano- and microscale and structural application. The deformation science and the role of nanotwins and dislocations in the presence of strain due to the presence of multicomponent solutes need to be understood. It was also realized whether HEAs can be effective in case of ceramic systems as well as other alloys where interstitial instead of substitutional elements are present. It has been recently emphasized[5] that the HEA-based design strategy should not be restricted to single-phase solid solutions alone, which has also emerged from the present workshop. It should be extended to a wide range of complex materials for exploiting the renaissance in physical metallurgy realized in recent times.

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Tropical ecology congress 2014*

The Tropical Ecology Congress (TEC) organized recently in New Delhi was attended by over 500 delegates, comprising more than 50 foreign delegates representing 17 countries. The congress was inaugurated by Skip Judson Van Bloem (Baruch Institute of Coastal Ecology and Forest Science, Clemson University, USA and the International Society for Tropical Ecology (ISTE)). The congress covered multiple dimensions of global change in a total of 21 technical sessions comprising 140 oral and 170 poster presentations, 7 plenary lectures, 3 panel discussions, and 2 special sessions. A panel of five experts reviewed the posters presented during the congress and selected the ten best among them. As expected, the impact of climate change was evident in many presentations and lectures. Furthermore, presentations addressed the current environmental problems such as disturbance, degradation of ecosystems, invasive species and water scarcity. That invasive species can also be useful in certain situations was an interesting conclusion of a study presented at the congress. Important conclusions include: understanding the environmental connections between the regions and their ecosystems could play a role in achieving issues of equity and justice; in developing countries environmental data are required not only for academic purpose, but also for realizing successful international negotiations and reducing conflicts; the payment for ecosystem services should be periodically analysed in view of scientific facts, though they may

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