# Dr. Daya Swarup Memorial Lecture 2023

## Multicomponent High Entropy Alloys: A Renaissance in Physical Metallurgy

## Prof. N. K. Mukhopadhyay

Department of Metallurgical Engineering Indian Institute of Technology (Banaras Hindu University) Varanasi 221 005



77<sup>th</sup> ANNUAL TECHNICAL MEETING KIIT, Bhubaneswar, 23<sup>rd</sup> November 2023

## The Indian Institute of Metals, Kolkata



## Dr. Daya Swarup

Dr Daya Swarup was Principal of the College of Mining and Metallurgy at BHU during 1942 and 1962, a crucial period in the history of the Institution. Following the advent Independence in August 1947, Dr Daya Swarup worked ceaselessly to emphasize the importance of the College and its importance and the role it was destined to play in free India.

For 34 years he worked as a Teacher out of which more than 20 years he was Head of the Metallurgical and Mining Departments. He secured grants from Universities and Government of India to equip laboratories and workshops of the College with latest equipments and instruments. He selected young teachers who had distinguished themselves in College, got them trained abroad, with the result that within a few years BHU had the best equipped Departments of Mining & Metallurgy in the Country.

There is no Mining and Metallurgical activity in India today, where his exstudents have a played a key and crucial role in Nation building activities be it in Steel, Non - Ferrous Metals, Mines or Engineering Industry.

In 1989, the Indian Institute of Metals instituted the Dr Daya Swarup Memorial Lecture to perpetuate the memory of a gifted teacher, a warmhearted person and an able administrator, who loved his profession and his students.

### Dr. Daya Swarup Memorial Lecture 2023

## Multicomponent High Entropy Alloys: A Renaissance in Physical Metallurgy

## N. K. Mukhopadhyay

Department of Metallurgical Engineering Indian Institute of Technology (Banaras Hindu University) Varanasi 221 005.UP. E-mail: <u>mukho.met@iitbhu.ac.in</u>

#### Introduction

I feel highly privileged and honored for being selected for delivering the 'Dr. Daya Swarup Memorial Lecture 2023' of the Indian Institute of Metals (IIM). I would like to express my sincere thanks to the IIM Council and the Award Committee for inviting me to deliver this lecture. Prof. Daya Swarup was the doyen of Metallurgical Education in India. I consider myself fortunate to be associated as a faculty member with the same Department where Dr. Daya Swarup (1904-1983) was an alumnus (1928) and a teacher. In fact, he was among the second batch of students completing undergraduate degree, B.Sc (Met. Engg.) in the Department under the Headship of Prof N.P. Gandhi. He served as a Professor and Head of Department (1937-1962), and Principal of the erstwhile College of Mining and Metallurgy (1944-62) of the Banaras Hindu University, Varanasi. He was responsible for the emergence of the Department as a postgraduate institution. During his tenure, the MSc (Met. Engg.) course was started in 1957 and the first ever Ph.D. (Met Engg.) degree in India was awarded in 1955. His efforts had acted as the guiding spirit for the Institute and paved the way to what it is today, Department of Metallurgical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi. Now, it is important to point out that the Department is observing the Centenary Celebration throughout the Year 2023. His books on metallurgy motivated and inspired metallurgists of that era all over India. In commemoration of Dr. Daya Swarup's seminal contributions to metallurgical education in India, in this presentation, I would like to share some of our interesting work related to the 'High Entropy Alloys', which have aroused a tremendous excitation among the Physical Metallurgists, Materials Scientists and Engineers to explore the various facets of this class of novel materials.

#### High Entropy Alloys (HEAs)

It is known that Physical Metallurgy deals with various issues of metallic alloys pertaining to the composition and processing routes leading to evolution of different phases having a variety of structures and microstructures and the resultant properties aimed at designing and developing

metallic alloys useful for technological applications. In 1926, the rules for the formation of a binary solid solution of metallic elements in a crystalline framework, which was considered as one of the important steps for successful alloy design, were proposed by William Hume-Rothery considering the atomic size, electronegativity, valence electrons and crystal structure of the individual metallic elements. Intermetallics or composites of immiscible elements are expected to form if the Hume-Rothery rules for solid solution formation are not satisfied. However, after the discovery of concentrated multicomponent solid solution alloys, there was a need to understand the principles underlying the formation of solid solutions containing five or more elements in high concentration. J. W. Yeh (Taiwan) first suggested that the stability of the solid solutions could be attributed to the high entropy arising due to randomness in the configuration of atoms in solid solutions. Thus, the concept of high entropy alloy (HEA) was advocated by him [1] in 2004, while interpreting the stabilization of these multicomponent equiatomic or near-equiatomic disordered solid solutions in metallic alloys. It is pertinent to point out that Brian Cantor (UK) independently worked on multicomponent alloys similar to HEAs since 1980 [2]. The multimetallic combination of metals was termed as 'multimetallic cocktails' by S. Ranganathan [3] 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 an alloy containing five or more elements with concentration ranging from 5% to 35% (at%), leading to a simple disordered solid solution structure. Interesting aspects of the work reported on HEAs are reviewed early in the book by Murty et al. [4].



**Figure 1:** The variation of configurational entropy ( $\Delta S_{conf}$ ) for an equimolar alloy with a number of elements.

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' [5]. Keeping in view the current excitement and interesting activities in this area, there are several thousands of published papers, many patents and also international workshops and conferences organized all over the globe. Earlier, S. Ranganathan [3] highlighted the multicomponent alloys in the context of bulk metallic glasses and HEAs. He emphasized the importance of cocktail effects in multimetallic alloys. He attributed cocktail effects in the multicomponent system to the extension of solid solution. In the literature reports on HEAs ranging from theoretical modeling and simulation, thermodynamics, synthesis, processing, characterization, property evaluation and possible applications. However, in addition to high entropy three other core effects such as sluggish diffusion, lattice distortion and cocktail effects were also proposed. Figure 1 discerns the variation of configurational entropy with respect to number of alloying elements in HEAs, the configurational entropy initially increases and then become almost stagnant.



Figure 2: The schematic representation of strained lattices in HEAs [6].

Due to various sizes of atoms in the multicomponent alloys, lattice is anticipated to highly strained and the schematic diagrams suggests typical strained lattices in HEAs [Figure 2]. Hence, the fundamental deformation science should be addressed differently in the context of HEAs unlike conventional alloys, involving three distinct factors encompassing strain rate dependence, role of nanotwinning and grain size dependence. It has been emphasized that the formation of nanocrystalline HEAs has made them more interesting due to their fundamental and technological

importance [7–9]. It has been elaborated the possible application (among various other applications) of HEAs should be explored in three niche areas – advanced ultra super critical (AUSC) coal-powered station, radiation environment, and aero-gas turbine engines [10,11]. Evaluating the data, it is suggested that for AUSCs the following components can be investigated: (i) oxide dispersion strengthened low stacking fault energy FCC alloys such as Cantor alloy i.e., CrMnFeCoNi with Y<sub>2</sub>O<sub>3</sub> dispersions; (ii) high-strength AlCrFeCoNi<sub>2</sub> 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<sub>0.4</sub> and Al<sub>0.3</sub>CrFeCoNi. For radiation environment with reference to fast breeder reactor fuel clad a combination of AlSiTiCrFeMo, not necessarily in equal atomic proportions, such that it leads to a low SFE BCC alloy with adequate ductility and strength to be explored. For high-pressure gas turbine rotors, a multiphase HEA from AlTiCrFeNiNbMo as well as VTaMoNbW may be worth considering.

## Low-density high entropy alloys (LDHEAs)

In recent times thrust for development of low-density high entropy alloys (LDHEAs) have gained impetuous for meeting the requirements of modern-day industry. Among the various classes of LDHEAs, the HEAs containing low-density elements like Mg, Al, Li, Ti, Be, Sc, Si etc. have gained some attention in recent times by the scientific community. A few researchers and co-workers have made significant efforts in understanding the microstructure and mechanical properties of LDHEAs containing elements like Sc, Be, Mg, Ti etc. The work of Vinod kumar and co-workers on LDHEAs needs special mention [12]. They have discerned the influence of elemental composition on the phase evolution, thermal stability and mechanical properties of Mg<sub>x</sub>AlCrFeCu (x = 0, 0.5, 1.0, 1.7 at%) LDHEAs prepared by milling and spark plasma sintering (SPS). The MA of AlCrFeCu and Mg<sub>0.5</sub>AlCrFeCu LDHEA for 20 h has led to the formation of a two-phase structure of BCC (major) and FCC (minor). Moreover, it has been observed that the lattice parameter of FCC is close to Cu. On increasing the amount of Mg in Mg<sub>x</sub>AlCrFeCu (x = 1.0, 1.7) LDHEA, two BCC phases were formed [12]. However, a more cost-effective alloy design strategy needs to be adopted for design and development of LDHEAs.

In the present lecture, I will be briefly discussing some of our recent work on MgAlSiCrFe, MgAlSiCrFeNi, MgAlSiCrFeCuZn, MgAlMnFeCu LDHEAs [13–16]. These LDHEAs were having experimental density in the range of 4 to 5.5 g.cm<sup>-3</sup>. These LDHEAs were prepared by mechanical alloying followed by spark plasma sintering (SPS) at 800 ° C. The alloying behavior, phase evolution, phase composition, and thermal stability of as-milled nanostructured LDHEAs powders were determined by X-ray diffraction techniques, transmission electron microscopy, scanning electron microscopy, and differential scanning calorimetry (DSC). The milling of elemental powders of

MgAlSiCrFe for 60 h led to the formation of HEA having BCC phase with a lattice parameter of 0.2887  $\pm$  0.005 nm (close to that of the  $\alpha$  -Fe) along with minor fraction of undissolved Si (Figure 3).



**Figure 3:** Phase evolution during mechanical alloying of MgAlSiCrFe high-entropy alloy milled up to 60 h [13].

The nanostructured HEA powders having crystallite size and grain size of ~19 nm was formed after milling. The STEM–EDS mapping of these milled powders confirms uniform elemental distribution following 60 h of MA (Figure 4). The DSC thermogram of 60 h milled HEA powder demonstrates the powder's thermal stability up to 400 °C. The exothermic heating events detected in the DSC thermogram correspond to phase transformation of MgAlSiCrFe HEA powder and may be corroborated with the phases observed in ex-situ XRD analysis of HEA powders annealed at various temperatures up to 700 °C. The systematic investigation discerns the presence of parent BCC phase along with other minor phases i.e. B2 type Al–Fe phase, FCC phases (Al–Mg solid solution), Cr<sub>5</sub>Si<sub>3</sub>, Mg<sub>2</sub>Si, and Al<sub>13</sub>Fe<sub>4</sub>. Additionally, this work correlates the experimental results with a variety of thermodynamic parameters in order to understand the phase evolution and stability. This work also showed the phase evolution, chemical composition, and microstructure of the SPSed

sample consolidated at 800 °C (1073 K) through XRD and SEM techniques. The SPSed samples exhibited the formation of B2-type AIFe phase (a=0.2889 nm) along with the parent disordered BCC phase and minor fraction of AI<sub>13</sub>Fe<sub>4</sub>,  $\beta$ -AI<sub>3</sub>Mg<sub>2</sub>, and Cr<sub>5</sub>Si<sub>3</sub>. The instrumented micro-indentation technique was used to examine the mechanical properties of the LDHEA. The hardness and yield strength were found to be approximately 7.0 GPa and 2.1 GPa with an appreciable relative density of 99.98% for the SPSed sample.



**Figure 4:** STEM–EDS mapping of equiatomic MgAlSiCrFe high-entropy alloy mechanically alloyed for 60 h showing homogenous elemental distribution[13].

The equiatomic MgAlSiCrFeNi LDHEA milled powder shows the formation of a BCC phase having lattice parameter of 0.2876±0.03 nm and undissolved Si (~3 at%) after 60 h of milling. The structural evolution and fine microstructural characteristics were examined under TEM (Figure 5). The micrographs showing bright field images (a, d) and selected area diffraction patterns (SADPs) (b, e), and dark field images (c, f) of 60 h MM powder reveals the presence of a BCC phase coexisting with the minor amount of undissolved Si. The bright-field image (Figure 5 (a)) reveals the heavy deformation induced during the MA and can be observed in the powder particle. The grains of  $\leq$  20 nm were also identified in the milled powder revealing considerable peak broadening. Figure 5(b), reveal the polycrystalline nature of the alloy by forming the ring pattern corresponding to the BCC phase. These rings are indexed as (110), (200), and (211) planes of BCC phase. Figure 5 (c) shows dark field image collected from the (110) plane, which confirms the nanocrystalline nature of the milled powder of sizes ~15 ± 4 nm.



**Figure 5:** TEM micrographs showing (a, d) bright field images and (b, e) selected area diffraction patterns and (c, f) dark field images of LDHEA powder milled after 60 h MM showing presence of BCC along with minor fraction of Si [15].

The DSC experiment up to 1200 °C (1473 K) shows five exothermic heating events (Figure 6) corresponding to various phase transformations, which were co-related with the results obtained from ex-situ XRD analysis of annealed powder at elevated temperatures (Figure 7). The phase transformation events during annealing at different temperature up to 800°C (1073 K) resulting in the formation of a major B2 type phase (a=0.289 nm) and BCC phase along with small amounts of FCC Al-Mg solid solution phase (FCC 1 (a=0.4082 nm) and FCC 2 (a=0.4215 nm)), monoclinic Al<sub>13</sub>Fe<sub>4</sub> (a=1.549 nm, b=0.808 nm, c=1.248 nm,  $\alpha$ = $\beta$ =90°), Mg<sub>2</sub>Si (a=0.6351 nm), Cr<sub>5</sub>Si<sub>3</sub> (a=b=0.9165 nm, c=0.4638 nm). The SPSed sample also exhibits BCC and B2-type phases coexisting with minor amounts of other phases observed for 800 °C (1073 K) annealed sample. In this work, it has been observed that the co-existence of minor phases with parent BCC phase in SPSed alloy (having

relative density of ~99.40%) has led to significantly high hardness and modulus of elasticity of ~9.98±0.3 GPa and 229±0.3 GPa respectively.



Figure 6: DSC thermogram of MgAlSiCrFeNi powder milled for 60 h exhibiting exothermic and endothermic events [15].



**Figure 7:** (a) Phase formation during annealing of 60 h milled MgAlSiCrFe HEA powder upto 800 °C (1073 K); (b) magnified image for (110) peak of the BCC phase for revealing evolution of other phases [15].

In continuation to the previous quaternary and hexanary LDHEAs, efforts were made to investigate the structure, microstructure and mechanical properties of equiatomic septenary MgAISiCrFeCuZn high entropy alloy synthesized by mechanical alloying for 60 h followed by spark

plasma sintering. The mechanical alloying led to the formation of major BCC phase (having lattice parameter of 0.2895 nm) with minor fraction of retained Si. The thermal stability of the milled powders was discerned through DSC thermogram up to 1200 °C (1473 K) and the various exothermic heating events observed were corroborated with the phases observed in the ex-situ XRD of annealed powders. The MgAlSiCrFeCuZn HEA was consolidated at 800 °C using SPS. The hardness and yield strength of SPSed samples were determined using instrumented instrumentation techniques. It was observed that for the conventionally sintered sample the hardness was ~6.0 GPa, however for the SPSed sample it was found to be ~9.0 GPa. The excellent indentation hardness may be due to the appreciable density of the SPSed sample.

Further, efforts were also made to synthesize and characterize low-density MgAlMnFeCu HEA. The low-density MgAlMnFeCu HEA has been synthesized by mechanical alloying (MA). Milling up to 60 h leads to the formation of a mixture of two phases consisting of a BCC phase (a =  $2.87 \pm 0.02$  Å) and  $\gamma$ -brass type phase (a =  $8.92 \pm 0.03$  Å), with ~2 µm powder particle size. The as-milled alloy after spark plasma sintering (SPS) at 900 °C exhibits an experimental density of 4.946 ± 0.13 g cc<sup>-1</sup>, which is 99.80% of the theoretical density. SPS leads to the formation of C15 Laves phase (MgCu<sub>2</sub> type; a =  $7.034 \pm 0.02$  Å) and B2 (AIFe type; (a =  $2.89 \pm 0.02$  Å) intermetallics along with the  $\gamma$ -brass type phase. The SPSed sample has exceptional hardness value (~5.06 GPa), high compressive strength (~1612 MPa) and appreciable failure strain (~6.4%) coupled with relatively low density.

The present work also focuses on calculating thermodynamic parameters, in order to correlate the experimental findings of phase evolution and stability of the annealed powder and spark plasma sintered quaternary, hexanary and septenary LDHEAs. The work also describes the phase evolution during MA and SPS using Thermo-Calc software with the help of property diagrams, which were generated through the CALPHAD approach. The phases observed experimentally and through property diagrams were not exactly correlated to each other. The main reason for this anomaly may be attributed to the absence of TCHEA database for HEAs containing low-density elements like Mg, Sc, Be etc.

#### High entropy steels

The surge for development of near or non-equiatomic high entropy alloys has led to conceptualization of high entropy steels (HES). This idea of HES was initially mooted by the Raabe and co-workers at MPIE, Germany in 2015 [17]. Most of the initial reports on HES have employed liquid metallurgical processing of fabrication of these materials. However, these routes often result in coarse microstructure accompanied with other issue pertaining to segregation, porosity etc. Here we will give an overview on the recent development of a few non-equiatomic Fe<sub>40</sub>Mn<sub>19</sub>Ni<sub>15</sub>Al<sub>15</sub>Si<sub>10</sub>C<sub>1</sub>

(at. %) [18]),  $Fe_{40}Mn_{14}Ni_{10}Cr_{10}Al_{15}Si_{10}C_1$  (at. %) [19],  $Fe_{40}Mn_{14}Ni_{10}Ti_{10}Al_{15}Si_{10}C_1$  (at. %) [20] high entropy steels prepared by mechanical alloying followed by spark plasma sintering. The  $Fe_{40}Mn_{19}Ni_{15}Al_{15}Si_{10}C_1$  (at. %) high entropy steel milled for 35 h results in the formation of multiphase structures i.e., a major BCC phase (a = 0.286 nm; cl2) along with minor fraction corresponding to  $\gamma$ brass type (a = 0.872 nm; cl52) and ordered B2-type (a = 0.290 nm; cP2) phases with the trace amount of retained Si as shown in the Figure 8.



Figure 8: (a) XRD patterns of the milled samples at various milling time; (b) Enlarged view in the range of 2θ (degree) = 49°-54°; (c) XRD pattern of the 35-h milled sample; (d) Rietveld refinement of the corresponding 35 h milled sample. This shows the alloying behavior of alloy as a function of milling time, and formation of the multi-phase structure (ferrite as a major phase) after 35 h of milling [18].

The milled powder was found to be thermally stable up to ~500 °C, however, the formation of Fe<sub>5</sub>Si<sub>3</sub>-type silicide phase was evident at ~520 °C. The spark plasma sintered (SPSed) sample was able to retain the BCC phase, B2 and  $\gamma$ -brass type along with the formation of Fe<sub>5</sub>Si<sub>3</sub> type silicide phase (a = b = 0.667 nm, c = 0.468 nm; hP16). These SPSed HES sample was found to have low density (~6.49 ± 0.3 g cm<sup>-3</sup>), high microhardness (~7.8 ± 0.3 GPa) and good compressive strength (~2046 ± 160 MPa) with an appreciable ductility of ~19% (Figure 9).



**Figure 9:** (a) Depth of penetration vs Indentation load (p-h plot); (b) Optical micrograph of the indent on SPSed HES sample; (c) Compressive engineering stress and strain curve; (d) Radar diagram showing comparison of different mechanical properties; (e and f) Comparition (microhardness vs density, and ultimate compressive stress vs density) of the present work with the conventional steel and other HEAs. This illustrate the physical and mechanical properties of the SPSed pellet [18].

The enhanced mechanical properties of the SPSed sample can be attributed to dual-phase microstructure i.e., BCC and B2 along with finer nano-sized silicide precipitates leading to dominant strengthening mechanisms (i.e., grain-boundary and dislocation strengthening). Further, these HES

has shown better wear resistance and biocompatibility in contrast to 316 L stainless steel. The specific wear rate of these HES was found to be  $\sim$ 1.79 x 10<sup>-5</sup> mm<sup>3</sup>/mN and better biocompatibility as compared with 316 L.

In contrast to the previous work, the 40 h milling of  $Fe_{40}Mn_{14}Ni_{10}Cr_{10}Al_{15}Si_{10}C_1$  high entropy steel led to the formation of a major BCC phase (a = 0.286 nm) and  $\chi$ -type phase (close to gamma brass structure). The milled powder sample showed the thermal stability up to 400 °C, then showed phase transformation at elevated temperatures. The FCC (a = 0.362 nm) and B2 (a = 0.290 nm) phases, along with Cr<sub>3</sub>Si (a = 0.455 nm) and Cr<sub>23</sub>C<sub>6</sub> (a =1.062 nm) precipitates formed after spark plasma sintering. The SPSed sample showed density of 6.8 g.cm<sup>-3</sup>. These SPSed HES also show excellent hardness (~7.4 GPa), good compressive strength (1962 MPa) and better wear properties (~0.99 x 10<sup>-5</sup> mm<sup>3</sup>.m<sup>-1</sup>N<sup>-1</sup>). Further this alloy exhibits better biocompatibility as compared to 316 L.

Similarly, efforts were made to understand the phase evolution, microstructure, thermal stability, mechanical and properties, and biocompatibility of the wear Fe<sub>40</sub>Mn<sub>14</sub>Ni<sub>10</sub>Ti<sub>10</sub>Al<sub>15</sub>Si<sub>10</sub>C<sub>1</sub> (at. %) high entropy steel. The 30-h milled powder was found to have a dual-phase containing a major BCC (a = 0.287 nm; cl2) and a y-brass type (a = 0.889 nm; cl52) phase having nanostructured grains of  $\sim 10 \pm 2$  nm. The differential scanning calorimetry (DSC) thermogram exhibited the four exothermic heating events at 530 °C, 690 °C, 860 °C and 1000 °C. The phase transformation corresponding to the heating events was correlated with the ex-situ XRD of the as-milled powder. The SPSed HES were found to have a dual-phase structure containing a major FCC phase (a = 0.362 nm; cF4) and a minor BCC phase along with the intermetallic phases like  $Fe_5Si_3$  type (a = b = 0.678 nm, c = 0.475 nm; hP16) and TiC (a = 0.431 nm; cF8). The mechanical properties of these SPSed samples were discerned through instrumented microhardness and compression tests. The microhardness, elastic modulus, ultimate compressive strength and strain were found to be ~10.4 GPa, ~209 GPa, ~2305 MPa and ~15% respectively. This SPSed HES showed an excellent room temperature microhardness and strength which can be attributed to the co-existence of FCC phase along with the minor BCC phase and hard intermetallics. The strengthening mechanism suggested that the grain boundary, dislocation, and precipitates strengthening were dominant. Further, wear and biocompatibility behaviour of the SPSed samples were done, and the specific wear rate is found to be  $1.62 \times 10^{-5} \text{ mm}^3/\text{mN}$  and better biocompatibility as compared with 316 L. These HES materials can be exploited for biomedical applications due to its excellent mechanical properties and biocompatilbity.

In view of the existing structure, microstructure, mechanical properties and biocompatibility exhibited by HES, further efforts were made to explore a few non-equiatomic Fe-based HEAs. These Fe-based HEAs having a nominal composition of  $Fe_{40}Mn_{20}Cr_{20-x}Ni_xTi_{10}AI_{10}$  (x = 0, 5, 10 at. %) HEAs were prepared by 40 h of MA followed by SPS. The 40-h milled Fe-based HEAs were found to have

a major along with minor fraction corresponding to  $\chi$ -type phase. The milled powder of Fe-based HEAs have discerned thermal stability up to 500 °C, and then formed FCC solid solution in all the three-alloy system. The BCC (major) phase transformed to dual phase i.e., FCC + BCC and further to FCC (major) phase as the Ni content increases from x = 0, 5, and 10 at. % after spark plasma sintering. The microhardness and yield strength values of the SPSed sample decreased from 6.4 GPa to 4.2 GPa, and 1961 MPa to 1300 MPa, respectively as the Ni content increased from x = 0 to 10 at. %. Further, these alloys showed better wear resistance and biocompatibility as compared to 316 L.

## Refractory high entropy of alloys

The refractory high entropy alloys (RHEAs) are an important class of HEAs mainly consisting of refractory elements like Ti, V, Cr, Zr, Nb, Mo, Y, W etc. In the year 2011, Senkov and Miracle [21] propagated the idea of RHEAs with their initial work on MoNbTaTiW based systems. Understanding the structure, microstructure, and thermal stability of these HEAs are of utmost importance for its potential application for high temperature structural materials. We will discuss the structural and microstructural stability in two RHEA systems from our work i.e. TiVZrMoW [22] and TiVZrYHf. The prediction of phases in TiVZrMoW RHEAs was attempted theoretically by following (i) Semi-empirical Miedema model, (ii) an 8 atom SQS generated using ATAT software, and the enthalpy of mixing value for the structure (FCC, BCC and HCP) calculated using DFT and (iii) CALPHAD approach. The as-cast alloy shows the presence of major BCC1 (a =  $3.17 \pm 0.02$  Å) being Mo and W rich and minor BCC2 (a =  $3.65 \pm 0.02$  Å) being Ti, Zr rich along with C15 type ternary Zr (Mo, W)<sub>2</sub> Laves phase (a =  $7.58 \pm 0.02$ Å).



**Figure 10**: STEM-EDS analysis of the as-cast powdered sample. The oval and rectangular area marked on Ti and Zr are showing lean regions in the elemental mapping [22].

Figure 10 discerns the elemental distribution of alloying elements in these RHEA. The Ti, Zr rich regions and Mo, W rich regions were clearly seen in the STEM-HAADF-EDS map. The DSC analysis of the as-cast sample shows two endothermic peaks of solid-solid transformation up to 620 °C. However, the alloy does not show any transformation in the temperature range of 620 - 1000 °C. The annealed sample (at 900 °C) shows that two BCC phases present in the as-cast sample were transformed into the ordered B2 structure.

The DFT approach in the study of phase stability of second refractory alloy, i.e., TiVZrYHf is a variation of cluster expansion method with fixed composition and cell size. Enthalpy of mixing of BCC and HCP structures were calculated for the distinct configuration of atoms on the lattice sites using a ten-atom cell. The annealed alloy was examined by XRD, SEM, and SEM-EDS. The annealed sample shows the presence of two disordered HCP1 (a =  $3.18 \pm 0.02$  Å, c/a = 1.58) and HCP2 (a =  $3.67 \pm 0.02$  Å, c/a = 1.55), along with BCC (a =  $3.16 \pm 0.02$  Å) and the ordered (Hf, Zr)V<sub>2</sub> (C15 type Laves phase, a =  $7.41 \pm 0.02$  Å) phase which is in accordance to the theoretically predicted phases. The SEM-EDS mapping of the annealed sample shows that the major HCP1 phase contains Hf and Zr predominantly along with some Ti.

#### Multi-component high entropy intermetallics and AI-HEA composites

This is a new class of HEAs, that has gained a lot attention off-late. Here, we will be discussing some of our recent work on multi-component high entropy intermetallics systems i.e., Laves phase, sigma phase, γ-brass alloys. The first report on the single-phase multi-component TiZrVCrNi high entropy Laves phase was reported earlier by us in 2017 [23,24]. This TiZrVCrNi HEA prepared by the conventional melting and casting as well as by the melt-spinning technique, exhibits micron size hexagonal C14 type Laves phase and nanocrystalline Laves phase respectively [23]. The detailed characterisation by X-ray diffraction, scanning and transmission electron microscopy and energydispersive X-ray spectroscopy confirmed the existence of a single-phase multi-component hexagonal C14-type Laves phase in all the as-cast, melt-spun and annealed alloys. The lattice parameter a = 5.08 Å and c = 8.41 Å was determined from the annealed material (annealing at 1173 K). The thermodynamic calculations following the Miedema's approach support the stability of the highentropy multicomponent Laves phase compared to that of the solid solution or glassy phases. These high entropy intermetallics represents excellent hardness (~8.92 GPa at 25 g load) for nanocrystalline high-entropy alloy ribbon without any visible signature of cracking. It implies that these high entropy intermetallics have a high-yield strength (~3.00 GPa) with reasonable fracture toughness. Further, we have investigated the hydrogen storage properties of TiZrVCrNi high entropy intermetallics [25]. The alloy investigated for hydrogen storage was synthesized by vacuum arc melting having a C14 type hexagonal Laves phase. The pressure composition isotherms (PCI) of this alloy were

investigated with pressure ranges at 0-40 atmosphere (Figure 11). The total hydrogen storage capacities were found to be 1.52 wt. %.



**Figure 11:** Hydrogenation curve of bulk as-cast  $Ti_{20}Zr_{20}V_{20}Cr_{20}Ni_{20}$  HEA, (b) TPD curves of hydrogenated kinetics curve of bulk as-cast  $Ti_{20}Zr_{20}V_{20}Cr_{20}Ni_{20}$  HEA, (c) pressure composition isotherm curve for absorption and desorption of bulk as-cast  $Ti_{20}Zr_{20}V_{20}Cr_{20}Ni_{20}$  HEA and (d) Number of Cycles *vs.* hydrogen storage capacity of bulk as-cast  $Ti_{20}Zr_{20}V_{20}Cr_{20}Ni_{20}$  HEAupto10 cycles [25].

The reversible hydrogen storage capacity was quite stable and only slight decreases in the storage capacity was observed after 10 cycles during hydrogen soaking. The demonstrations of hydrogen storage capacity of the TiZrVCrNi equiatomic alloy were found to be very promising and surge the path for potential hydrogen storage application of these high entropy intermetallics with Laves phases.

The multi-component  $\sigma$ -phase (sigma phase) were observed in Cantor based HEAs prepared by mechanical alloying followed by pressure-less sintering at elevated temperatures in CrMnFeCoMo system. The 40 h milling resulted in the formation of two solid solution phases with BCC structure (a= 3.146 ± 0.002 Å and 2.873 ± 0.002 Å) along with minor amount of retained  $\alpha$ -Mn [26]. Phase formation, chemical composition, thermal stability etc. were also evaluated using electron microscopy and differential thermal analysis (DTA) methods as well as in-situ high temperature x-ray diffraction technique. The pressure-less sintered sample exhibited four phases i.e. two BCC solid solution,  $\sigma$  (sigma) and  $\mu$  (mu), which were found to be stable until melting of these alloys. The phase formation was predicted by Thermo-Calc approach and was compared with the experimental observation as well as other calculated results. The sintered samples were tested by instrumented hardness tester for evaluation of mechanical properties, and was found to exhibit high hardness (9.3 ± 0.3 GPa) and Young's modulus (~245 ± 6 GPa).

Similarly, effort was made to synthesize AI- HEA (AISiCrMnFeNiCu) composite by powder metallurgy route. The high entropy (AISiCrMnFeNiCu) phase was found to have a major B2-type phase (a=0.29 nm; cP2) along with a minor phase corresponding to Cr<sub>5</sub>Si<sub>3</sub>-type silicide (a=b=0.9165 nm, c=0.4638 nm; tI32). These high entropy aluminides were found to have excellent hardness (~7 GPa) with a low-density of 5.08 g.cm<sup>-3</sup>, making them lucrative to be exploited as a reinforcement for AI matrix composites. We have demonstrated the synthesis of 6082 AI matrix composite reinforced with AISiCrMnFeNiCu high entropy aluminide by mechanical milling followed by pressure-less sintering. Mechanical milling (MM) imparts significant refinement, and nanostructuring of grains (~10– 12 nm) for AI based nanocomposite powder was observed (Figure 12).



**Figure 12:** TEM micrograph of AI-30HEA nanocomposite showing the (a) bright-field image (b) corresponding selected area diffraction pattern, (c)dark field image, and (d) grain size distribution in nanocomposites [27].

These powders of AI based nanocomposite was found to be thermally stable up to 650 °C. Further, these AI-HEA nanocomposite powders were consolidated through pressure-less sintering at



560 °C, which led to the formation of a thin  $\sim$ 400–500 nm transitional layer at the interface. The microhardness of these AMCs was tuned in the range of  $\sim$ 0.90 to 1.81 GPa.

**Figure 13:** SEM micrograph of (a & d) AI-10HEA, (b & e) AI-20HEA, (c & f) AI-30HEA consolidated by pressure-less sintering at different magnification. (g) SEM–EDS mapping of AI-30HEA composite consolidated by pressure-less sintering showing the formation of transitional layer and elemental distribution. (h) Load versus indentation depth plot for AI-HEA composite. Optical micrograph for the indentation on (i) AI-10HEA (j) AI-20HEA, and (k) AI-30HEA pressure-less sintered composite [27].

#### Fe-based medium entropy alloys

At the early stage of the development of high-entropy alloys (HEAs), the focus was centered on producing alloys with simple solid solution phases of BCC, FCC and HCP phases to utilize the concept of configurational entropy. Later on, it was realized that the maximization of the configurational entropy through the equiatomic composition of the constituent elements is not the sole parameter to form the random solid solution. The non-equiatomic alloy composition provides more flexibility in designing the new alloys in the vast composition space and utilizes the effect of chemical composition on the microstructural evolution, which will lead to enhanced properties. This also allows designing alloys to reduce the material cost, to meet the applicability of these alloys.

In this regard, the element Fe draws more attention due to conventional Fe-based alloys have shown an excellent set of properties. With this objective, we have developed two Fe-based medium entropy alloys (MEAs) of 1.5 Kg weight each through vacuum induction melting furnace. The first composition of Fe<sub>40</sub>Cr<sub>25</sub>Ni<sub>15</sub>Al<sub>15</sub>Co<sub>5</sub> MEA in the as-cast state has shown the two-phase structure of Fe-Cr rich BCC phase and Ni-Al rich ordered B2 phase. The bright field and corresponding selected area diffraction (SAD) pattern of the as-cast alloy are given in Figure 14. The cuboidal B2 precipitates of sizes 100-200 nm are embedded within the disordered BCC matrix. In the diffraction pattern (Figure 14 (b)), a cubic pattern with a four-fold rotation symmetry is easily discerned. Additionally, modulation of intensity among the diffraction spots are present which may be due to the partial or complete ordering of either the B2/BCC phase or both phases simultaneously.



**Figure 14:** (a) Bright field electron micrograph and (b) selected area diffraction pattern (SAD) of ascast  $Fe_{40}Cr_{25}Ni_{15}AI_{15}Co_5$  MEA. Cuboidal B2 precipitates are embedded in the BCC-disordered matrix. (c) & (d) bright and dark field images of B2 precipitates within the disordered BCC matrix [28].

The orientation relationship is [100] of the B2 phase is parallel to the [100] of the BCC phase and the [110] of the B2 phase is parallel to the [110] of the BCC phase. This is commonly known as a cube-on-cube orientation relationship with no in-plane rotation. Under this situation, the interface between the cuboid and the matrix is likely to be (100) type. A closer view of the B2 precipitates with the BCC matrix can be seen through a magnified image (Figure 14 (c)). Figure 14 (c & d) shows the bright field and dark field imaging of the B2 precipitate with the matrix. The presence of the dislocation lines could be observed in the B2 phase and the BCC matrix in the bright field as well as in the dark field image. The appearance of the dislocation lines indicates that they are most likely mixed type. The presence of the thickness fringes at the interface of the cuboids further confirms the polyhedral nature of the precipitates. While some of the dislocations end at the BCC-B2 interface, some dislocations do cross over the interface. This is probably due to the semi-coherent nature of the interface.



Figure 15: X-ray diffraction patterns of (a) as-cast and (b) heat-treated samples at 600 °C (873K), 900 °C (1173 K) - 2h & 800° C (1073 K) for 12h and cooled down in a furnace [28].

The phase stability of the alloy was studied by exposing the as-cast alloy at different temperatures. Figure 15 shows the multiple displays of X-ray diffraction patterns at different time-temperature scales. It can be seen that at 600 °C (873K) there was no change in the phase observed except the increase in intensities of the peaks. This may happen due to the release of the crystal strain during the heat treatment of the alloy. Further increase in heating temperature at 800 °C (1173K), shows the increase in the intensity of the first superlattice reflection (100) of the B2 phase, relative to the as-cast structure.

This suggests that with the increase in heat treatment temperature degree of ordering increases. It means the volume fraction of the B2 phase is increased. The thermal stability of the evolved phases was further investigated at a longer holding time of 12h at 800 °C (1073K). There was no sign of phase transformation that could be observed even at a longer holding time. The diffraction pattern corresponding to this temperature showed all the reflections of the B2 phase. Therefore, it is imperative to say that the B2-type ordered phase is stable over a higher time-temperature range. The alloy is found to have a yield strength of ~ 1012 MPa and an ultimate compressive strength of ~1405 MPa. The yield strength of the studied alloy is comparatively higher than some of the earlier reported HEAs, but the alloy lacks plasticity. This may be due to the presence of the brittle Ni-Al-based B2-type intermetallic phase.

In the second composition of Fe<sub>50</sub>Mn<sub>20</sub>Al<sub>15</sub>Ni<sub>10</sub>Co<sub>5</sub> MEA, we incorporate the Mn to further reduce the cost and induce the FCC phase-forming ability of the alloy. The as-cast alloy shows the BCC/B2 phase along with the formation of the FCC phase near the grain boundary area. Figure 3 shows the high-magnification SEM micrographs. The marked areas, near the grain boundary and in the matrix (white contrast) region, in Figure 16 (a) were magnified. The region near the grain boundary has black contrast and appears in the form of fine leafs (figure 16 (b). This might be the case of the rejection of Fe and Mn elements during the formation of Al-Ni-rich B2 precipitates in the BCC matrix. The formation of FCC (dark contrast) would lead to the rejection of Al and Ni into the matrix, which favours the B2 phase formation. A closer look at the same magnified area in Figure 16 (c) further reveals that the regions away from the dark area possess very fine structures. Similarly, a high magnification micrograph of the white matrix region (marked with a circle in Figure 16 (a)) depicts a modulated structure of densely formed B2 precipitates in the BCC matrix (figure 16 (d and e)). The SEM-EDS line analysis through the modulated structure confirms the Ni-Al-rich composition of the B2 precipitates (Figure 16 (f)).



**Figure 16:** The high-resolution SEM micrographs of as-cast Fe<sub>50</sub>Mn<sub>20</sub>Al<sub>15</sub>Ni<sub>10</sub>Co<sub>5</sub> MEA. Marked rectangular FCC region magnified in (b) and (c). Marked circular BCC region magnified in (d, e and f). The EDS shown in the insert of (f) indicates the formation of the Ni-Al-rich B2 phase [29].



**Figure 17:** The bright field images (a and b) and selected area diffraction pattern of the marked area in (b) of as-cast Fe<sub>50</sub>Mn<sub>20</sub>Al<sub>15</sub>Ni<sub>10</sub>Co<sub>5</sub> MEA. The high magnification bright field and dark field image of the marked area in (a). B2 precipitates of varying sizes of range 80-100 nm could be observed in the BCC matrix [29].

Figure 17 shows the TEM bright field (BF) and dark field (DF) micrographs and the corresponding selected area diffraction (SAD) patterns of the alloy. The elongated grains of width in the sub-micron range and dark regions in the marked grains indicate the presence of defects in the alloy (Figures 17 (a) and (b)). The SAD patterns of the marked areas confirm the formation of ordered B2 (a= 2.93Å) and disordered BCC (a= 2.96Å) phase (Figure 17 (b) inset image). The marked area in the BF image (Figure 17(a)) indicates the formation of B2 precipitates in the BCC matrix. The dark field image shows that the width of B2 precipitates varies in the range of 80-120 nm of different shapes. The chemical compositions of ordered B2 precipitates in the disordered BCC matrix were confirmed through the STEM-EDS elemental maps. Figure 18 shows the STEM BF micrograph and corresponding elemental maps of Fe, Mn, Al, Ni and Co elements. It shows that B2 precipitates are significantly enriched in Ni and Al elements and depleted in Fe and Mn. Moreover, Co is uniformly distributed in both phases though with a slight enrichment in the B2 phase.



**Figure 18:** The STEM-EDS elemental maps of the as-cast Fe<sub>50</sub>Mn<sub>20</sub>Al<sub>15</sub>Ni<sub>10</sub>Co<sub>5</sub> MEA. The B2 precipitates richer in Ni and Al, and the BCC matrix richer in Fe and Mn could be depicted. However, Co is ingressed in both phases [29].

The mechanical properties of the as-cast alloy were evaluated at room temperature in terms of compression behvaiour and hardness. The alloy demonstrates the yield and ultimate compressive strength of ~1250 MPa and ~1675 MPa, respectively, with compressive ductility of ~42%. The alloy exhibited a high hardness value of ~450 HV in the as-cast condition. These above results have shown the partial substitution of constituent elements into Fe, provides immense opportunities to design the alloys for high-temperature applications along with balance of strength and ductility. Although the

cost of the Fe-based MEAs is still higher compared to the conventional steel, it has shown a relatively lower cost compared to the other equiatomic HEAs and MEAs. The development of Fe-based MEAs has given a potential direction for the future development of MEAs to meet the industrial application of these alloys.

## **Concluding Remarks**

While designing alloys suitable for technological applications based on structural and functional properties, it is suggested that HEAs could be taken as the base alloy and then minor additions could be made to obtain the desired microstructure and mechanical properties for improving the stability and the properties. It is important to emphasize that attention of materials researchers have been focused at the central or near central region of the phase diagram, which was otherwise grossly ignored so far except a few cases. However, it has also raised the question of the effective role and ability of configurational entropy to stabilize the useful solid solubility range of the disordered solid solution phases. It has now become clear that the alloy design strategy of combining multiple elements in near-equiatomic or non-equiatomic proportions with single or multi-phase combination 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 applications. The deformation science and the role of nanotwins and dislocations in the presence of strain due to multicomponent solutes need to be understood. It has been recently emphasized that the HEA-based design strategy should not be restricted to single-phase solid solutions alone and it should be extended to a wide range of complex phases including intermetallics as well as developing composites for exploiting the renaissance in physical metallurgy realized in recent times. In order to reap the benefit of this new class of materials, it has been suggested to explore the possible application of HEAs in three strategic areas - advanced ultra super critical (AUSC) coal-powered station, radiation environment, and aero-gas turbine engines. There are also attempts being pursued to develop high entropy ceramics and polymeric materials and composites for enhanced structural and functional properties and their applications. It is anticipated that these continuous and intense research efforts on multiprincipal multielement materials will lead to advance our fundamental understanding on the concentrated alloys and also to develop some useful materials for the niche applications.

## Acknowledgements

I would like to record my deep sense of gratitude to Prof. S. Ranganathan, Prof. K. Chattopadhyay, Prof S. Lele, (Late) Prof. O.N. Srivastava, (Late) R. Krishnan, Prof. I. Manna, and Prof. B.S. Murty for their continuous encouragements and support throughout my academic journey. My heartfelt thanks are due to all my collaborators and colleagues, especially, Prof. R.K. Mandal, Prof. B.N. Sarma, Dr. Joysurya Basu, Dr. R. Manna, Dr. Kausik Chattopadhyay, Dr. T.P Yadav and Dr. V.C. Srivastava for their active collaboration and many stimulating discussions. I also wish to convey my sincere thanks to all my former and current students who were the driving force to motivate me to continue the work, especially, Dr. Vikas Shivam, Dr. Vivek Pandey, Dr. Nandini Singh, Dr. Yagnesh Shadangi, Mr. Harsh Jain, Mr. Priyotosh Pradhan, Mr. Abhisek Singh, Mr. Ritik Roshan Tripathy, and Mr. Rajat Gupta. I thankfully acknowledge the efforts of Dr, Yagnesh Shadangi and Dr. Vikas Shivam in assisting me to prepare this article. On this occasion, I would like to thank my wife, Prof. Santwana Mukhopadhyay and my daughter, Semanti and also other family members for their continuing support, understanding and adjustments during all seasons of my life.

## References (selected)

- [1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes, Adv. Eng. Mater. 6 (2004) 299–303.
- [2] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. A. 375–377 (2004) 213–218.
- [3] S. Ranganathan, Alloyed pleasures: Multiatomic cocktails, Curr. Sci. 85 (2003) 1404–1406.
- [4] B.S. Murty, J.W. Yeh, S. Ranganathan, High Entropy Alloys, Butterworth-Heinemann, 2014.
- [5] N.K Mukhopadhyay, High entropy alloys: a renaissance in physical metallurgy, Curr. Sci. 109 (2015) 665–667.
- [6] J.W. Yeh, Alloy design strategies and future trends in high-entropy alloys, JOM. 65 (2013) 1759–1771.
- [7] M. Vaidya, G.M. Muralikrishna, B.S. Murty, High-entropy alloys by mechanical alloying: A review, J. Mater. Res. 34 (2019) 664–686.
- [8] V. Shivam, J. Basu, V.K. Pandey, Y. Shadangi, N.K. Mukhopadhyay, Alloying behaviour, thermal stability and phase evolution in quinary AlCoCrFeNi high entropy alloy, Adv. Powder Technol. 29 (2018) 2221–2230.

- [9] V. Shivam, J. Basu, Y. Shadangi, M.K. Singh, N.K. Mukhopadhyay, Mechano-chemical synthesis, thermal stability and phase evolution in AlCoCrFeNiMn high entropy alloy, J. Alloys Compd. **757** (2018) 87–97.
- [10] A. Kareer, J.C. Waite, B. Li, A. Couet, D.E.J. Armstrong, A.J. Wilkinson, Short communication :
  'Low activation , refractory , high entropy alloys for nuclear applications ,' J. Nucl. Mater. 526 (2019) 1–6.
- [11] B. Cao, T. Yang, W. Liu, C.T. Liu, Precipitation-hardened high-entropy alloys for high-temperature applications : A critical review, MRS Bull. **44** (2019) 854–859.
- [12] O. Maulik, D. Kumar, S. Kumar, D.M. Fabijanic, V. Kumar, Intermetallics Structural evolution of spark plasma sintered AlFeCuCrMg x (x=0, 0.5,1.0, 1.7) high entropy alloys, 77 (2016) 46– 56.
- [13] N. Singh, Y. Shadangi, G.S. Goud, V.K. Pandey, V. Shivam, N.K. Mukhopadhyay, Fabrication of MgAlSiCrFe Low-Density High-Entropy Alloy by Mechanical Alloying and Spark Plasma Sintering, Trans. Indian Inst. Met. **74** (2021) 2203–2219.
- [14] N. Singh, Y. Shadangi, N. Krishna, Phase Evolution and Thermal Stability of Low-Density MgAlSiCrFe High-Entropy Alloy Processed Through Mechanical Alloying, Trans. Indian Inst. Met. **73** (2020) 2377–2386.
- [15] N. Singh, Y. Shadangi, V. Shivam, N.K. Mukhopadhyay, MgAlSiCrFeNi low-density high entropy alloy processed by mechanical alloying and spark plasma sintering: Effect on phase evolution and thermal stability, J. Alloys Compd. 875 (2021) 159923.
- [16] V.K. Pandey, Y. Shadangi, V. Shivam, J. Basu, K. Chattopadhyay, B. Majumdar, B.N. Sarma, N.K. Mukhopadhyay, Synthesis, Characterization and Thermal Stability of Nanocrystalline MgAIMnFeCu Low-Density High-Entropy Alloy, Trans. Indian Inst. Met. **74** (2021) 33–44.
- [17] D. Raabe, C.C. Tasan, H. Springer, M. Bausch, From High-Entropy Alloys to High-Entropy Steels, Steel Res. Int. 86 (2015) 1127–1138.
- [18] H. Jain, Y. Shadangi, D. Chakravarty, K. Chattopadhyay, A.K. Dubey, N.K. Mukhopadhyay, Low-density Fe40Mn19Ni15Al15Si10C1 high entropy steel processed by mechanical alloying and spark plasma sintering: Phase evolution, microstructure and mechanical properties, Mater. Sci. Eng. A. 869 (2023) 144776.
- [19] H. Jain, Y. Shadangi, V. Shivam, D. Chakravarty, Dibyendu Mukhopadhya, N.K Kumar, Phase evolution and mechanical properties of non-equiatomic Fe-Mn-Ni-Cr-Al-Si-C high entropy steel, J. Alloys Compd. 834 (2020) 155013.
- [20] H. Jain, Y. Shadangi, D. Chakravarty, A.K. Dubey, N.K. Mukhopadhyay, High entropy steel processed through mechanical alloying and spark plasma sintering: Alloying behaviour, thermal stability and mechanical properties, Mater. Sci. Eng. A. 856 (2022) 144029.

- [21] O.N. Senkov, G.B. Wilks, J.M. Scott, D.B. Miracle, Mechanical properties of Nb 25 Mo 25 Ta 25 W 25 and V 20 Nb 20 Mo 20 Ta 20 W 20 refractory high entropy alloys, Intermetallics. 19 (2011) 698–706.
- [22] V.K. Pandey, Y. Shadangi, V. Shivam, B.N. Sarma, N.K. Mukhopadhyay, Theoretical and experimental study on phase stability of TiVZrMoW refractory high entropy alloy, Philos. Mag. 102 (2022) 480–503.
- [23] T.P. Yadav, S. Mukhopadhyay, S.S. Mishra, N.K. Mukhopadhyay, O.N. Srivastava, Synthesis of a single phase of high-entropy Laves intermetallics in the Ti–Zr–V–Cr–Ni equiatomic alloy, Philos. Mag. Lett. 97 (2017) 494–503.
- [24] O.N. Senkov, G.B. Wilks, D.B. Miracle, C.P. Chuang, P.K. Liaw, Intermetallics Refractory highentropy alloys, Intermetallics. 18 (2010) 1758–1765.
- [25] A. Kumar, T. Prasad, N. Krishna, Notable hydrogen storage in Ti-Zr-V-Cr-Ni high entropy alloy, Int. J. Hydrogen Energy. 47 (2022) 22893–22900.
- [26] P. Pradhan, Y. Shadangi, V. Shivam, N.K. Mukhopadhyay, Powder metallurgical processing of CrMnFeCoMo high entropy alloy\_ Phase evolution, microstructure, thermal stability and mechanical properties, J. Alloys Compd. **935** (2023) 168002.
- [27] Y. Shadangi, K. Chattopadhyay, N.K. Mukhopadhyay, Powder metallurgical processing of Al matrix composite reinforced with AlSiCrMnFeNiCu high-entropy alloys: Microstructure, thermal stability, and microhardness, J. Mater. Res. 38 (2023) 248–264.
- [28] V. Shivam, J. Basu, R. Manna, N.K. Mukhopadhyay, Local Composition Migration Induced Microstructural Evolution and Mechanical Properties of Non-equiatomic Fe40Cr25Ni15Al15Co5 Medium-Entropy Alloy, Metall. Mater. Trans. A. 52 (2021) 1777–1789.
- [29] V. Shivam, S. Kar, G.K. Bansal, A.K. Chandan, B.K. Sahoo, G.K. Mandal, N.K. Mukhopadhyay, V.C. Srivastava, A novel Fe-rich non-equiatomic medium-entropy alloy with superior mechanical properties, J. Alloys Compd. **952** (2023) 170029.

Professor N. K. Mukhopadhyay (born on August 5, 1962) started his career in Metallurgical Engineering from Bengal Engineering College of Calcutta University (1983), now known as IIEST, Shibpur. He obtained his M.E. (1985) and Ph.D. (1990) from Indian Institute of Science, Bangalore. After his postdoctoral research at McMaster University, Canada (1990-1994), he joined CSIR-National Metallurgical Laboratory, Jamshedpur in 1994 as Scientist and then moved to Institute of Technology (BHU), Varanasi (now known as Indian Institute of Technology (BHU), Varanasi) in 1998 as Reader and became Professor in 2006 in the Department of Metallurgical



Engineering, IIT (BHU) Varanasi. Presently, he is serving the Department as Professor (HAG) since August 2012. He also was Head of Department between 2017-2020. He has visited TU-Dresden, Germany as Alexander von Humboldt Fellow and also as a visiting Scientist/Professor at various international institutions such as IFW (Dresden, Germany), McMaster University (Canada), Yonsai University (S. Korea).

Prof. Mukhopadhyay has received several prestigious awards/honors such as the INSA Gold Medal for Young Scientists (1990) awarded by the Indian National Science Academy, New Delhi, ALEXANDER von HUMBOLDT Fellowship, Germany (2003), the prestigious National Metallurgists' Day Awards: 'Metallurgist of the year' in 2006 from the Ministry of Steel, Govt. of India, 'Mishra Award' by Institution of Minerals Engineers and 'Nijhawan Award' by CSIR-National Metallurgical Laboratory, Jamshedpur. He also received 'MRSI Medal for 2008' from Materials Research Society (MRSI). He is a recipient of Prof. C.N.R. Rao Education Foundation Award in 2010. He has been elected as Fellow of Indian National Academy of Engineering (FNAE) in 2009, Fellow of Institution of Engineers (FIE) in 2003, the Indian Institute of Metals (FIIM) in 2007, Electron Microscope Society of India (FEMSI) in 2013, and Fellow of West Bengal Academy of Science & Technology (FAScT) in 2015 and Fellow of Asia Pacific Academy of Materials (FAPAM), and Fellow of the National Academy of Sciences, India (FNASc), Allahabad in 2021. He has been recipient of INAE Chair Professorship Award (2015-2016). He has been felicitated by the Institution of Engineers (India), Kolkata as 'Eminent Materials Engineer-2010'. He has been awarded IIM-G.D. Birla Gold Medal (2016) and 'Distinguished Educator' (2018) by Indian Institute of Metals. He was awarded ASM-IIM visiting Lectureship and under this program he visited in 2015 University of Utah, Salt Lake City, USA. He has delivered Prof A.K. Seal Memorial Lecture (2009) of Institution of Engineers (India). He has been selected for delivering 'Dr. Daya Swarup Memorial' Lecture of Indian Institute of Metals (2023). He is recipient of 'Lifetime Achievement Award' from Electron Microscope Society of India (EMSI) for his outstanding contribution on electron microscopy of Quasicrystals. Recently, he has been elected as a Fellow of Indian National Science Academy (FNA) (2023).

He is a member of International Advisory Board of 'Quasicrystals' since 2008 and 'Mechanochemistry and Mechanical Alloying' since 2003. He has also been elected as a member of the commission of '*Aperiodic Crystals*' of International Union of Crystallography (IUCr), UK since 2008. Earlier he served as consultant of '*Electron Diffraction*' commission of IUCr, UK. He is serving on the editorial board of various International Journals such as *Metallurgical and Materials Transaction A* as Key Reader since 2008 and as an editor of *Metallurgy and Materials Journal (Series D)* of Institution of Engineers (India), and guest editor for *Journal of Alloys and Compounds*. Recently, he has been invited to join as an Editor of the *Transactions of the Indian Institute of Metals* (Springer) and Associate Editor of *Journal of Alloys and Metallurgical Systems* (Elsevier).

Prof. Mukhopadhyay has made several outstanding contributions in the areas of quasicrystals (QC), complex metallic alloys, nanomaterials, mechanical milling, nanoindentation, and failure analysis. He has published over 250 papers in international journals of repute and delivered more than 50 lectures as an invited speaker and chaired technical sessions in many national/ international Conferences. He visited several countries including USA, Canada, UK, Germany, France, Switzerland, Israel, South Korea, China and Japan in connection with collaborative research projects as well as participation in international conferences.