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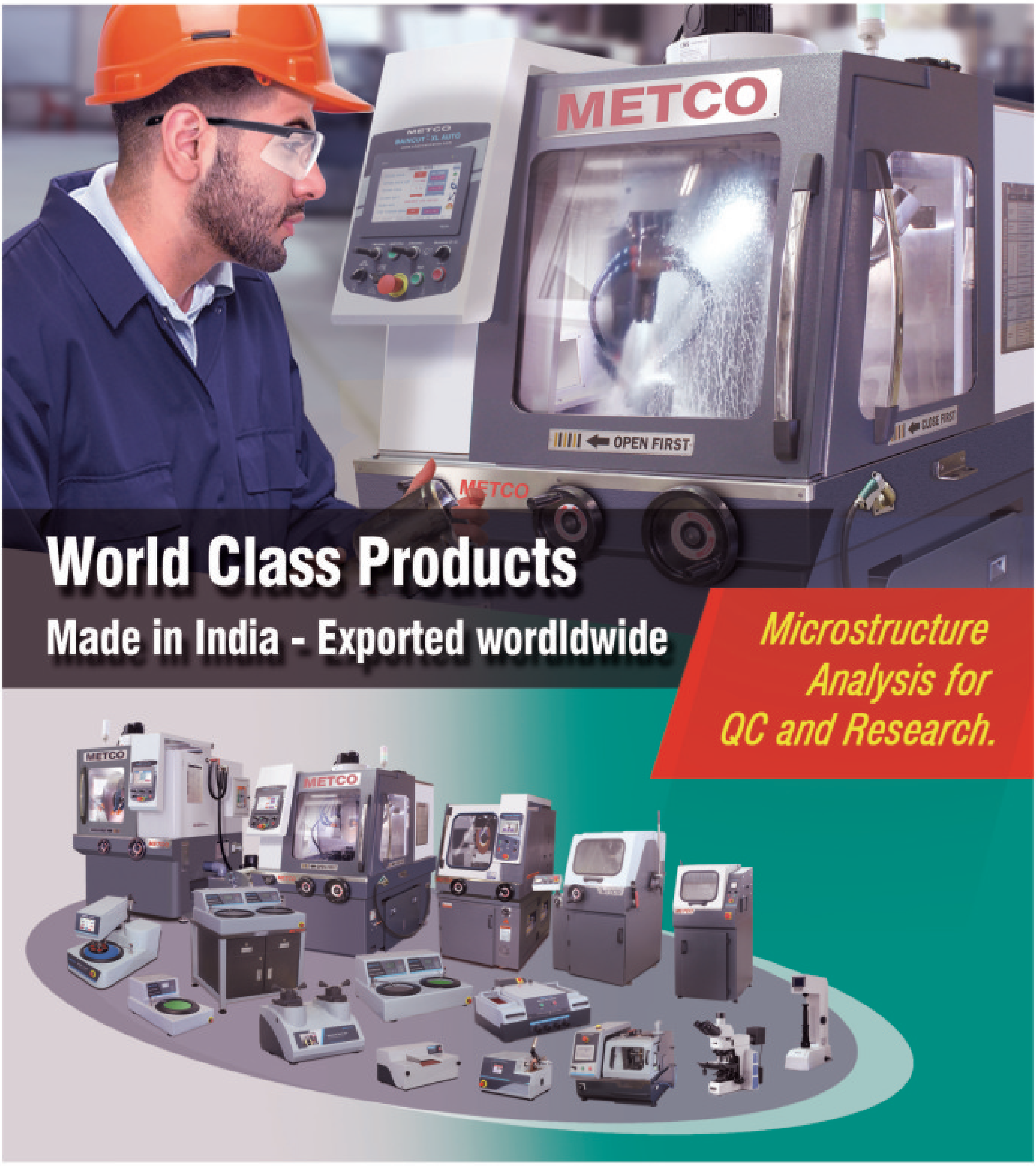
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CONTENTS

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Iron-containing Complex Concentrated Alloys: Next Gen Materials

Saumya R Jha and Krishanu Biswas[#]

Abstract

Conventional dilute alloys reign the overall consumption of alloys and materials throughout the world to the extent that per capita steel production forms an integral parameter for GDP estimation. However, with the advent of the novel concept of high-entropy alloys and complex concentrated alloys, these alloy systems have recently received tremendous attention in the community of metallurgy and materials engineering. In fact, the studies on high-entropy steels have emerged as an altogether new domain in the ferrous sector, with substantial improvement in properties and tunability. Unlike dilute alloys, these concentrated alloy systems incorporate the synergy of multiple strengthening mechanisms, making them useful for a variety of structural applications. The current review describes the evolution of this class of materials, with a perspective on novel-alloy design strategies for the development of iron-containing complex concentrated alloys.

Keywords : Complex concentrated alloy, High entropy steels, Mechanical properties, Functional Properties, Tribology, Corrosion, Design Philosophy.

1. History of Conventional alloys: an era overseen by steels

Centuries of sustained advancements in the materials domain have led to the development of several important engineering alloys for diverse applications, triggered primarily by the discovery of the fact that significant strengthening effect can be achieved via small elemental additions with variety of microstructural engineering techniques [1]. The first alloy serendipitously discovered using this idea in the pre-historic times was bronze, wherein a small quantity of tin was alloyed into a matrix of copper. Iron was slowly replaced by bronze alloys as engineering materials used for strategic applications, which was then succeeded by steels, synthesized again serendipitously by adding minor amounts of Carbon in an Iron base [2]. Several alloys involving other base elements like titanium, aluminum, nickel, zinc, magnesium etc. were thereafter discovered and used for specific engineering applications. For instance, duralumin, which belongs to the 2XXX series of aluminum alloys, wherein the base element is alloyed with small amount of copper, making the matrix a supersaturated solid solution, upon serendipitous heat treatment, displayed age-hardening behavior unlocking additional strengthening response to those known at the time. However, steels reigned the overall arena of specialized and generic applications, which ranged from structural applications in the construction industry to automobile sector, as well as ordinance and household items. Blending trace amounts of other elements conferred additional properties in steels, leading to the development of major classes of popular and reliable steels. For example, alloying of chromium and nickel gives rise to stainless steels (*e.g.* – Fe-18Cr-8Ni), which were used for various corrosion resistant applications. With the conception of the dislocation theory, the deformation behavior of varieties of steels were investigated and manipulated to obtain desirable

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properties. In the ulterior length scale, from the crystallographic perspective, iron can take two crystalline forms, *i.e.*, body centered cubic (alpha) at lower temperatures and face centered cubic (gamma) at elevated temperatures. Steels being interstitial solid solutions, the ferritic and austenitic phases also possess the similar crystallographic configuration as those of alpha and gamma iron, respectively. Probing the thermodynamic stability of the steels and stable crystallographic forms, researchers were keen on developing processing routes for dynamic tunability with regard to thermomechanical processing, giving rise to the concept of TTT (Temperature-Time- Transformation) and CCT (Continuous Cooling Transformation) diagrams. With the advent of these charts and allied experimentation on the variation of isothermal and continuous cooling rates, additional phases like martensite and bainite were discovered, revolutionizing the steel industry with tougher steel grades and remarkably stronger steels like maraging steel, which is considered as one of the highly regarded alloys in the known materials domain. Depending on the relative proportions of these phases and morphology, influenced by the microalloying constituents, steels were classified into various grades, so much so that, currently there are over 3500 grades according to the World Steel Association. For centuries, immense research went into devising processing and compositional parameters for specialized steels, through which novel grades were standardized into several internationally acclaimed standards, *viz*, BIS, AISI, SAE, EU, ASTM, etc. As for example, SAE grade 304 stainless steel is commonly used in boilers, pipelines, crockery, automobiles and several other places. Similarly, grade 316 austenitic steel has found versatile applications in pharmaceutical industry, jet engines, valves, exchangers, evaporators, furnaces, etc. Owing to exceptional toughness, maraging steel grade C300 has also found application in aircraft landing gears, transmissions shafts, tools and ordinance, etc. Once a pioneering sector for multiscale research, with huge industrialization and commercialization, the ferrous domain has been found to reach saturation in terms of new alloy chemistry and advancement of properties, owing to the dilute nature of this class of alloys. The lure of this class of alloys was reinstated by research in high entropy steels, which is now a flourishing field in the materials science arena. The current perspective is devoted to the discussion on iron containing high entropy alloy, evolution, interesting mechanical and functional properties and future scope of these complex concentrated alloys (CCAs).

2. Concentrated alloy systems

Over and above the age-old and widely used concept of dilute alloys, the novel concept of concentrated alloys for design of new alloys is fundamentally built on the Hume-Rothery principles for the formation of stable solid solutions, leading to a paradigm shift in the materials research community. They became widely popular with the discovery of the Cantor alloy being the first high entropy alloy, wherein simple crystalline phase with FCC structure stabilizes over the complex metastable phases, reportedly owing to higher configurational mixing entropy in multi-principle multi-component alloys [3]. Lately, several comprehensive reviews have been published in this field [4–10]. Traditional believers have often questioned the novelty of this concept, as superalloys have long been known to materials community as comprising large number of alloying additions, possessing relatively higher configurational entropy [11]. However, inarguably, they do not fall into the category of CCAs in principle, as they still have a base element, such as Nickel, Iron, Cobalt etc. Nonetheless, research in this domain has led to discovery of many potent iron-containing alloy systems, such as $FeCrNiCoAl_x$, FeMnNi, FeNiCoCu, FeMnCoCr, $Fe_{55}Mn_{15}Ni_{15}Co_{15}$, FeNiCo, FeCrNiAl, $Fe_{40}Mn_{40}Cr_{10}Co_{10}$, FeMnNiCoCu etc. Most of these have iron as the major constituent, imbibing the effects of strengthening similar to those in steels. Encompassing these, a novel class of high entropy steels has also been developed, wherein iron can be considered to be the 'major' component while other alloying elements are also added in significantly higher proportions than in conventional steels. These even include systems like the Fe-Mn-Al-Si-C, Fe-Mn-Al-C, or Fe-Co-Cr-Mn-B, containing both substitutional as well as interstitial element, and demonstrated superior yield strength, compressive strength, strain hardening, high strain rate and low temperature ductility with impressive plasticity and damage tolerance owing to multiple planar slip with profuse shear banding [12]. The compositional diversity and enormity derived from various permutations of elements in assorted proportions yield a huge variety of alloy systems using interstitial and substitutional solutes in the solvent matrix. Thus, the advent of such a vast class with cosmic scale of possibilities opens up routes to design and develop alloys of high specifications and exercise a better control and modifying the microstructure and properties.

3. Properties of Iron-containing Complex Concentrated Alloys

3.1 Mechanical Properties

The mechanical behavior of these alloys is largely influenced by the predominance of phases formed and the microstructure. The significant factors for phase stabilization include alloy chemistry, thermodynamic parameters like mixing entropy, enthalpy of mixing, valence electron concentration and electro-negativity difference, etc. [13]. Apart from the compositional aspects, the microstructure is significantly governed by the synthesis and processing routes. Researchers have adopted various routes such as casting, powder metallurgy, and additive manufacturing to develop these alloys and study the influence of processing variables alongside their properties. Of late, several material databases are available which compile the properties of almost all investigated concentrated alloy systems so far, providing yield strength, hardness, elongation, tensile strength, Poisson's ratio, elastic modulus, shear modulus, compressive strength, fracture toughness, etc. A few remarkable iron-based systems include FeMnNiCoCr, CoCrFeNiTi, $Al_{0.7}Co_{0.3}CrFeNi$, FeMnNiCoCu, which display a tensile strength over 2 GPa achieved with suitable processing [14,15]. Fig. 1 summarizes the current know-how of the concentrated alloy systems with regard to their mechanical properties.

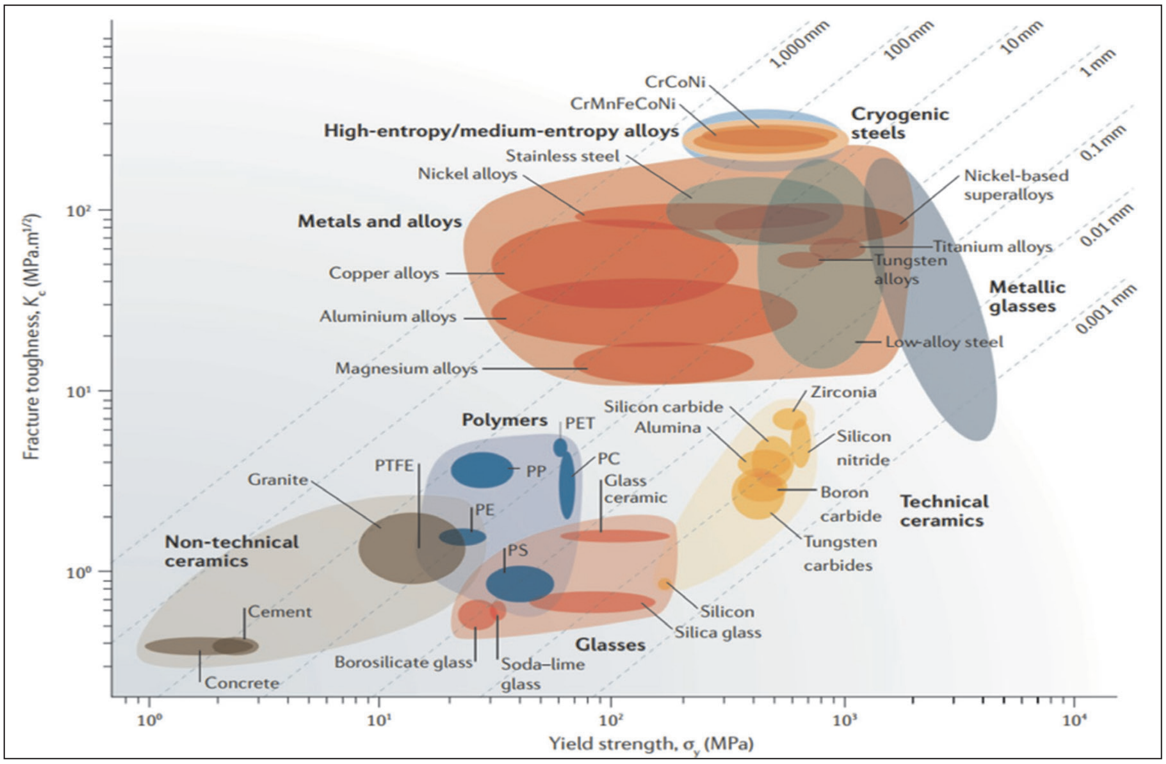

Fig. 1 : Fracture toughness vs yield strength data charted on property maps for conventional materials demonstrating superiority of CCAs [16,17] (Liu et al, Metals, 2021)

Reportedly, many such alloys also exhibit occurrence of multiple phases which adds another dimension to the strengthening, in addition to other mechanisms like solid solution strengthening, grain boundary strengthening, lattice friction strengthening and strain hardening. Several low stacking fault energy (SFE) alloys also show twinning wherein enormous strength-ductility synergy is observed owing to operation of multiple deformation modes and dynamic Hall-Petch effect surrounding the twin boundaries and CSL boundaries [18]. Articulate microstructures depicting intense deformation twinning are found to develop in case of a low SFE concentrated alloy of FeMnNiCoCr (≈ 25 mJ/m^2) in the cryogenic temperature, the mechanism commonly referred to as Twinning induced plasticity (TWIP). A similar heterostructure can be obtained *via* Transformation induced plasticity (TRIP) in CoCrNi and several low SFE CCAs. Needless to say, these additional strengthening mechanisms confer further improvement of mechanical properties, hinting at another important factor pertaining to microstructural control via SFE engineering. A recent study reflects on the effect of strain, strain rate and temperature on the kinetics of deformation in FCC complex concentrated systems [19]. Fig. 2 provides an aesthetic visualization of deformation twinning and serration at the vicinity of crack-tip under plane strain condition in Cantor alloy.

A unique and distinct strengthening mechanism observed in case of such concentrated ultralow SFE CCAs like $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ is the bidirectional transformation induced plasticity (B-TRIP) effect, wherein multiple forward and reverse FCC/HCP transformation is achieved by dynamic deformation, enabling higher refinement and work-hardening characteristics in a dual phase complex concentrated system [21]. A comprehensive illustration of comparative trends in the stress-strain behavior of TRIP/TWIP iron based HEAs with respect to Hadfield steel is shown in Fig. 3.

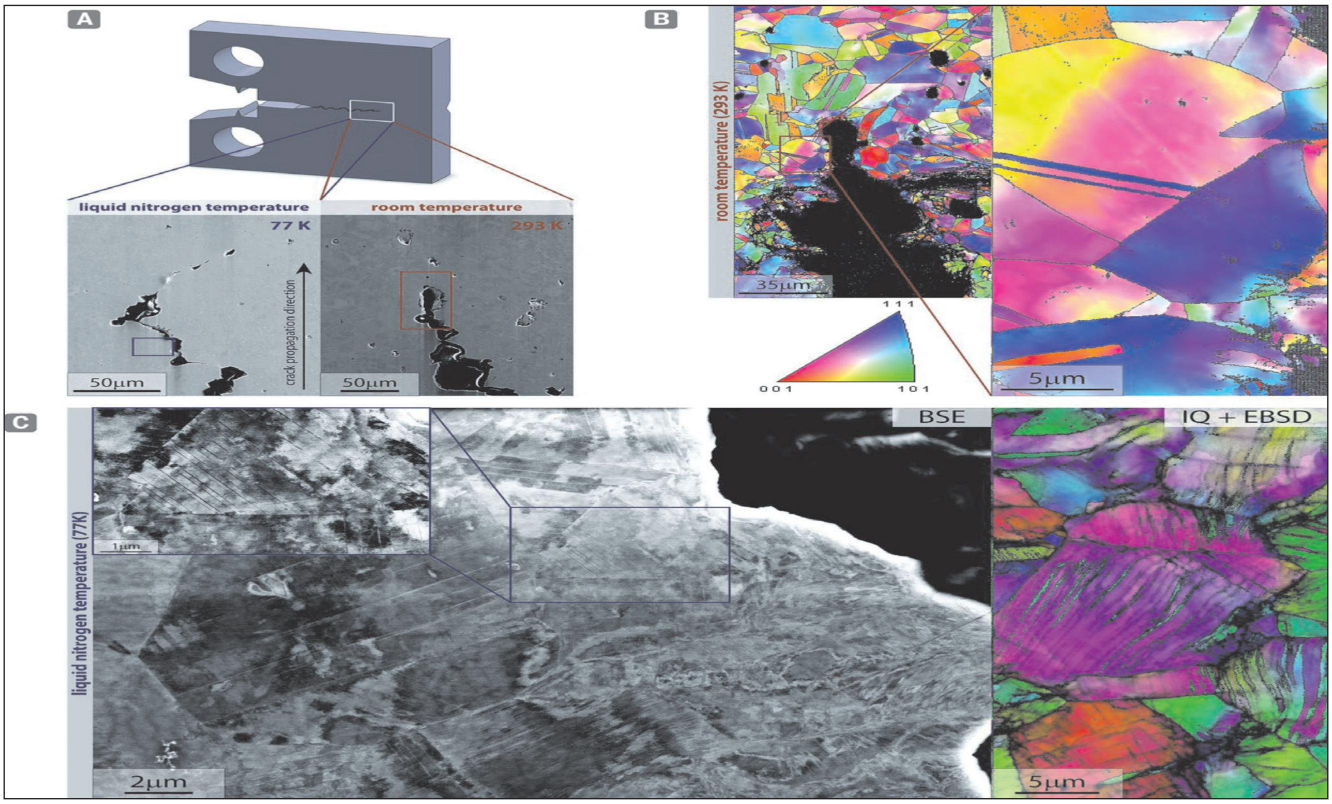

Fig. 2 : (a) SEM micrographs in the locality of crack-tip showing ductile mode fracture in Cantor alloy with corresponding EBSD images at (b) room temperature and (c) cryogenic temperature [20] (Bernd et al, Science, 2014)

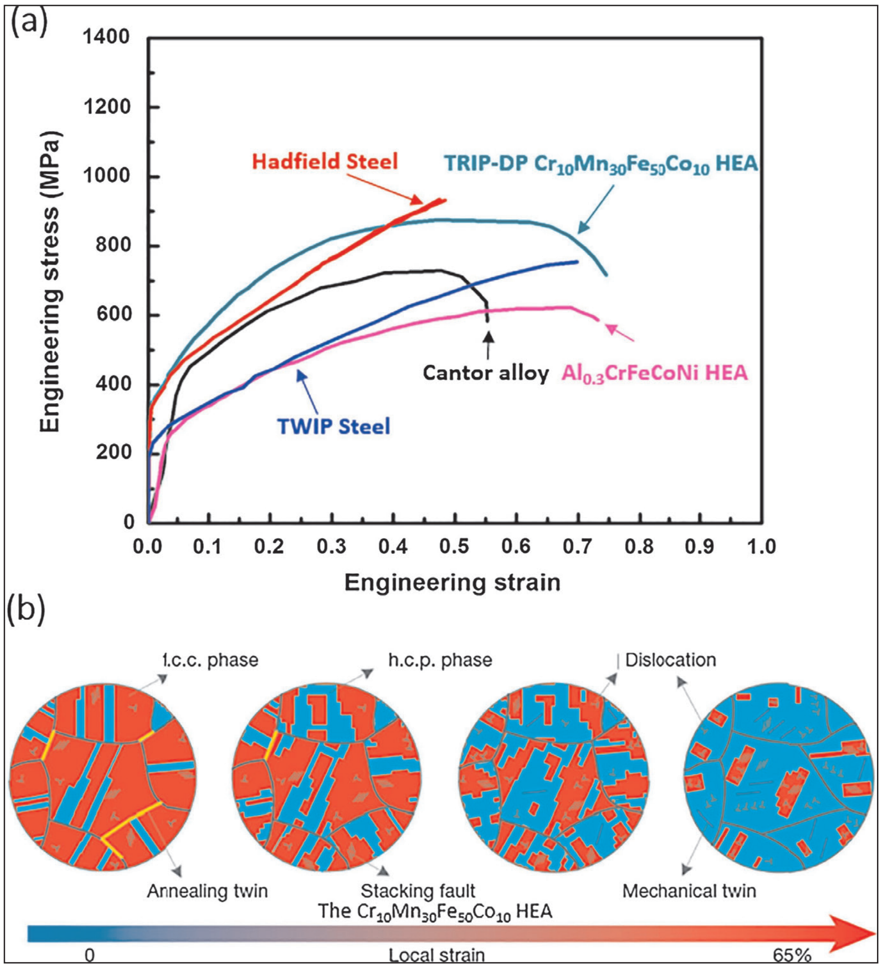

Fig. 3 : (a) Stress-strain plots aside (b) schematic microstructural representation in Cantor alloy and iron-based TWIP/TRIP HEAs [22] (Li et al, Prog. Mater. Sci, 2019)

Other scopes on microstructural engineering explored till now include developing multimodal and gradient microstructures, laminate structures or harmonic structures, strategically targeting the stress-strain partitioning to incorporate higher plasticity along with superior strain hardening. Harping on grain boundary strengthening characteristics, a recent study adroitly investigated the effect of microstructural heterogeneity in a single phase CCA over its mechanical behavior through microstructure entropy parameter [23]. Also, in such systems, the effect of short-range ordering (SRO) has been admittedly found to have significant contribution towards the improvement of mechanical properties, as that of dispersion strengthening.

3.2 Functional Properties

Although few studies have been reported to probe the CCAs on magneto-caloric properties, thermal conductivity, thermo-electric properties, electrical resistivity, superconducting as well as hydrogen storage, not enough evidence substantiates a general superiority of them over the existing traditional alloys in this domain. However, there exist clear indicators that CCAs are 'minefields' to be investigated for the search of materials with improved properties. As opposed to the popular Fe- or Co- containing magnets made of NdFeB and SmCo, CCAs offer a wider scope to design rare earth-free magnetic materials, as they derive coercivity from spinodal segregation into interconnected hard and soft phases [24]. Fig. 4 summarizes the remnant induction vs. coercivity values for a few CCA magnetic materials against traditional ones.

Several iron-containing CCAs, viz like $FeCoNiMn_{0.25}Al_{0.25}$, FeNiCoCrCu and FeMnNiCoCr

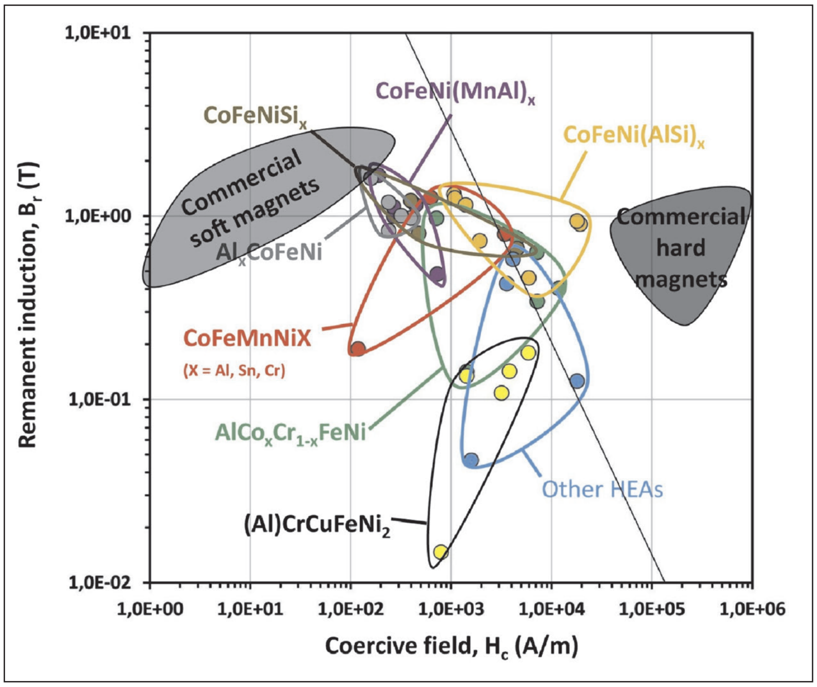

Fig. 4 : Ashby map for remnant induction magnetization vs. magnetic coercivity for CCAs vs commercial conventional magnets [1] (Gorsse et al., Comptes Rendus Phys, 2018)

have sought attention of the materials community due to their soft magnetic properties along with excellent thermal stability at elevated temperatures [25]. Factors including alloy base, solute incorporated, phases formed and relative volume fraction of the phases hold a vivid impact on the magnetic properties of the synthesized CCA. In fact, the implications of the phase formation are such that, FeCoCrNiAl$_x$ is found to transform from paramagnetic (FCC) to ferromagnetic (BCC), upon change in the crystal structure due to Al content (x=0 to x=2) [26]. Ascending over allied properties, these materials may have newfound applications in power grid, signal-processing equipment and even transducers. Particularly, a group of FeCoNi(AlSi)$_x$ (x ≤ 8) alloys have been found to exhibit electrical resistance values in the range of those of silicon steels and even higher [27]. High electrical resistivities in soft magnets play significant roles in minimizing eddy current losses, making these iron containing CCAs exemplary for potential magnetic and electrical applications. Compared to FCC CCAs, scarce literature is available on BCC CCAs most of which are deemed as refractory materials suitable for high temperature applications. Light-weighting is an important aspect indicated by high specific strength values of these alloys, see Fig. 5.

Although there is dearth of reports on the deformation behavior of most refractory iron containing CCAs, selective ones like TiZrHfNbFe alloys, which exhibit BCC + Laves phase, have been probed for their compressive properties as well as dry and wet corrosive wear resistance, even better than Ti6Al4V [28]. These resuscitate them as potent implant materials for biomedical applications, as cheaper alternatives. In addition, FeCrMoNbTaTiZr, FeMoCrNbTaTi, FeMoCrNbTaZr, FeMoCrTaTiZr, FeCrTaNbTiZr, and FeTaNbTiZrMo alloys have also been proven as potent biocompatible materials [29]. Many other characteristics like catalytic and surface adsorption are also important functional properties. Hydrogen storage is one amongst the most prominent applications directly aligned along these parameters. DFT calculations corroborated by experimental evidences yield the hydrogen adsorption measured by HER activity, portray the quaternary alloy of FeCoCrNi comparable to that of Pt, showing the overpotential being nominally higher than that of Pt [30].

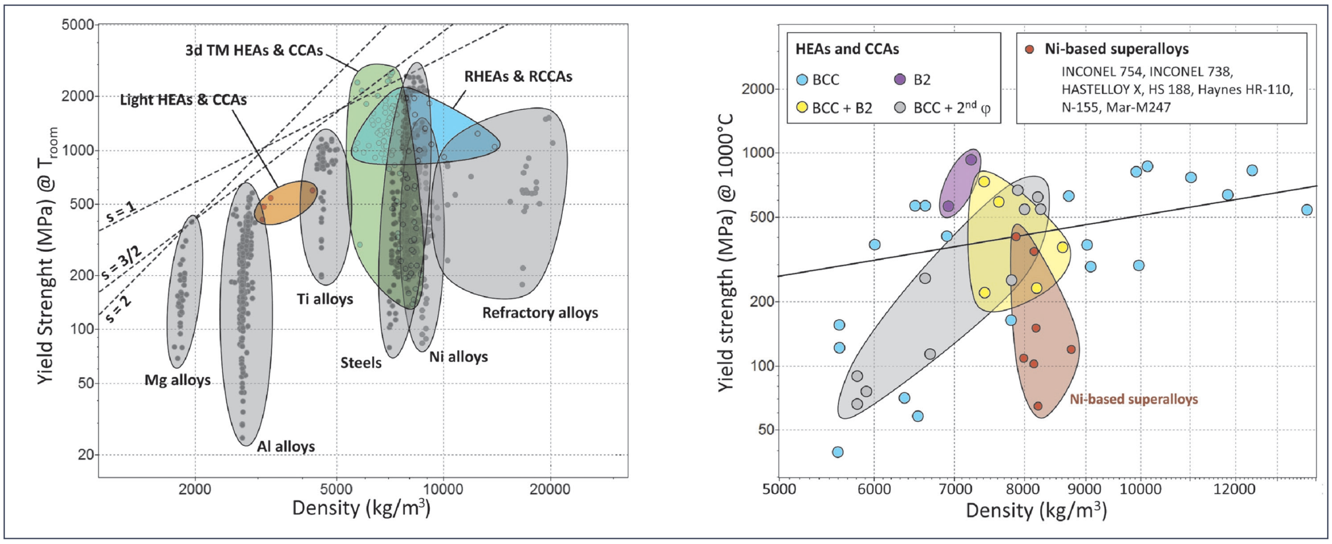

Fig. 5. Ashby maps of various complex concentrated alloys against traditional materials at room temperature and high temperatures showing high specific strength [1] (Gorsse et al., Comptes Rendus Phys, 2018)

3.3 Tribological and corrosion properties

In generic terms, BCC CCAs possess better wear resistance as compared to their FCC and FCC+BCC counterparts, which is mainly due to their higher hardness and compressive strength. FeCoCrNi$Ti_{0.5}$Al, Fe_2AlCoCr$Mo_{0.5}$Ni, and FeCoCrNiMnAl are some of the BCC iron based CCAs while FeCoCrNi$Al_{0.6}$, FeCoNiCuAl and FeAlCoCrNi are a few FCC iron containing CCAs exhibiting relatively lower dry sliding wear rates [31]. For such concentrated alloy systems, VEC < 6.87 leads to the formation of BCC phase, desirable in terms of tribology. Hsu et al. carried out a detailed study on the effect of iron additions on the improvement in wear properties of AlCoCr$Mo_{0.5}$Ni alloy, primarily owing to strong oxide layer formation [32]. According to Guo's VEC theory, alloy combinations with VEC in the range of 6.87 and 8 majorly produce FCC+BCC phases, which is desirable for utilizing the benefits of both the worlds, *i.e*, high plasticity of FCC with the high wear resistance of BCC [33]. A detailed analysis for establishing the temperature dependence of the surface hardness also testified BCC materials like FeCoCrMnNi$Al_{1.0}$, FeNiAlCoCr and few others to be markedly higher in terms of hardness, compared to Inconel 718 and austenitic steels for a large span of temperatures [31]. Further improvement on the wear resistance can be achieved by incorporating phase or phases, providing lubricating behavior in the materials during service. This, in general, is possibly attained either by using soft and low melting point metals and metalloids (Pb, Sn etc) or polymer in HEA matrix. Yadav et al. have demonstrated the use of Pb, Bi, Sn in substantial improvement of the wear resistance of CuCrFeTiZn and AlCrFeMnV HEAs due to self-lubricating behavior [34,35]. These metallic second phase become soft and behave like lubricating films during usage, providing lubrication. Furthermore, self-lubricating HEA composites were formulated by Zhang et al by reinforcing Ni-coated MoS_2 and graphite into a matrix of quaternary FeCoCrNi alloy [36]. The attempts to engineer iron- based CCA composites with solid lubricants like graphene or MoS_2 have revealed better wear resistance with lower coefficient of friction [37]. Interestingly, FeNiCoCrCu has also been explored to describe the lubricating nature of copper and sulphur from MoS_2 in minute proportions [38,39], in addition to anti-wear properties of Ni and Co in an iron base [36]. Nevertheless, despite impressive tribological improvements, FeNiCoCrCu_x alloy showed a decrease in passivation with increase in Cu-content in the aqueous NaCl solution [40]. The last decade has seen an exorbitant rise in the studies related to corrosion properties of CCAs and the effects of their exposure to aqueous corrosive media, such as saline water, acids, and high temperature/pressure or aggravated environment conditions. Fig. 6 highlights the active corrosion resistance in CCAs against several conventional alloys with respect to standard calomel and hydrogen electrodes upon prolonged exposure to corrosive NaCl and acidic H_2SO_4 media.

Effect of elemental additions such as Al in $Fe_{1.5}CrMnNi_{0.5}Al_x$ CCA in potentio-dynamic polarization provided enhanced resistance to pitting corrosion due to strong passivation [42]. Other elements like Ni, Mo, Cr etc were also alloyed with iron in non-equiatomic combinations to obtain enhanced passivation in many concentrated systems [43,44], simultaneously displaying better thermal stability, fatigue and fracture properties in several instances. To make them economically viable and cost effective, the current focus has shifted to developing high entropy coatings for bulk materials, showing superior corrosion properties, using magnetron sputtering, laser cladding or electrospark deposition [45–48]. Stable passivating HEA films possess a characteristically strong ionic resistivity to prevent surface and subsurface electrochemical activity: an example being high cavitation and erosion corrosion resistance of 304 stainless steel using laser-alloyed HEA film [49].

4. Design Philosophy and the use of computational tools

Designing of alloys, forms a key aspect in engineering a given material, be it alloys, ceramics, composites, thin films, or polymers. In totality, it refers to the overall choice or modulation of material chemistry, followed by pre-processing and treatments used to derive desired properties on the basis of the prior obtained data, as well as individual elemental properties. Unlike the traditional dilute alloys, where the solute concentration limitation curtails the design spectrum, CCAs hold a great degree of freedom and flexibility to choose from a large palette of elements over vast regimes of the compositions. However, designing also relates to meso-scale microstructural modulation, which is similar to the case of conventional alloys, involving controls using grain boundary engineering, SFE engineering, secondary phases, etc. This can remarkably impact the properties. On simplistic terms, strength-ductility trade-off being one of the major limitations in structural material design, can be largely overcome by utilizing multimodal, harmonic or gradient microstructures even in a simple single phase alloy [50–53]. Having no definitive grounds for designing parameters per se, it includes, in general, all factors which can be maneuvered to tune the properties of

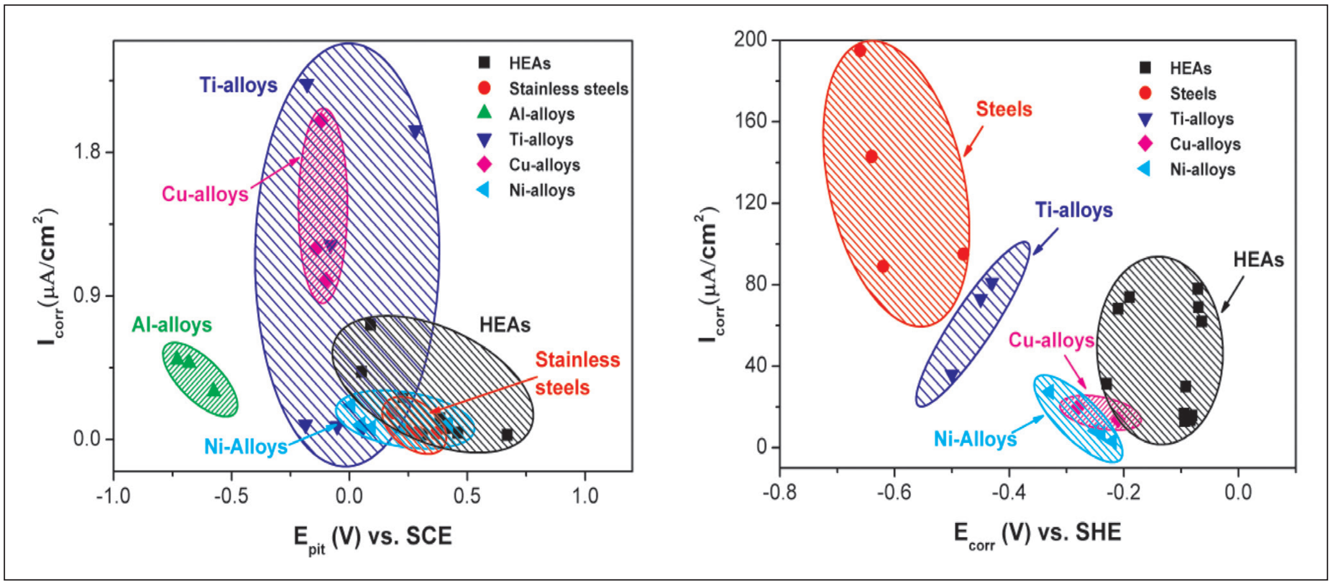

Fig. 6 : I_{corr} vs E_{corr} charts for HEAs vs conventional materials showing low corrosion current values for most concentrated alloy systems [41] (Shi et al, Metals, 2017)

any given material. As for CCAs, predictions using thermodynamic variables and parametric approaches based on enthalpy and free energy data using Miedema's model were primarily used for screening, which was later packaged into modules of CALPHAD technique for phase diagram predictions, and thereby, pave ways for unearthing novel alloy combinations based on thermodynamic analyses [54]. Advancing ahead, researchers also started using *ab initio* calculations using DFT principles, MD or FEM/FFT simulations to predict not just the chemistry, but also processing variables enroute to obtaining desired properties, which can incorporate thermomechanical treatments, doping, etc. Thus, process control is also now a major contributor to designing of any alloy system. Post the serendipitous discovery of the Cantor alloy, there are numerous iron-based CCAs, which not only are admirable in terms of properties, but also in many cases, fairly economical substitutes for several existing materials today. With the advent of improved machine learning tools and enhanced computational capability to handle large chunks of data, researchers are now also exploring the arena of concentrated alloy development on robust models of machine learning, unlocking the potential to unveil unexplored alloys in the materials space. An exemplary work carried out in this direction is the design of HCP concentrated alloy based on the robust extra tree (ET) classifier tool using machine learning [55,56].

Conclusion and Way Forward

Since antiquity, steels have been known, studied, experimented and evolved as important engineering materials for many applications. They have constituted as integral components in the materials usage. However, a large portion of the materials universe is yet unrealized, and holds immense possibilities for development of novel engineering materials for strategic applications. Complex concentrated alloys unveiled undiscovered regions in the phase space, shifting the focus of the materials scientists from dilute to concentrated alloy systems. Nonetheless, a thorough review of the state-of-the-art literature projects iron-containing concentrated alloys to possess tremendous potential in terms of maneuverability and properties. The vast expanse of compositional and entropic freedom in the realm of such alloys leads to possibilities of several synchronous strengthening mechanisms at play, and many other factors operative for the observed enhancement in properties. Therefore, it is expected that further research into this field shall discover and design more useful engineering materials for mankind, which were not possible under several constraints in the realm of dilute systems. However, despite unfolding enormous possibilities of alloy combinations, a major gap lies in devising hunting tactics for the desired traits, as experimental synthesis and analyses for each system is extensive and demanding in terms of resources. As a rejoinder, scientists have devised high-throughput experimentation and computational screening schemes based on existing databases. Moreover, regression-based analyses and AI-based smart software with enhanced predictive capabilities are forthcoming imminent platforms, which are increasingly becoming popular now-a-days. Although data on these alloys available in current literature are pretty limited, bootstrapping and extrapolative algorithms have laid the foundation for developing synthetic data on the basis of simulation and experimental outcomes. Research in this domain is supposed to largely depend on such predictive tools for reducing the dependence on experiments.

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A Brief Write–up on Non-Isothermal Devolatilization of Coal

A Ghosh

Introduction

S. K. Dutta [1] investigated non-isothermal reduction of composite pellets of iron ore – coal / char and also carried out study of non-isothermal devolatilization of coal. Only a part of it has been published [2,3]. The present paper also includes reports of a few other studies of non-isothermal devolatilization of coal [4,5] and is a brief write –up on the subject based on the above and some other sources.

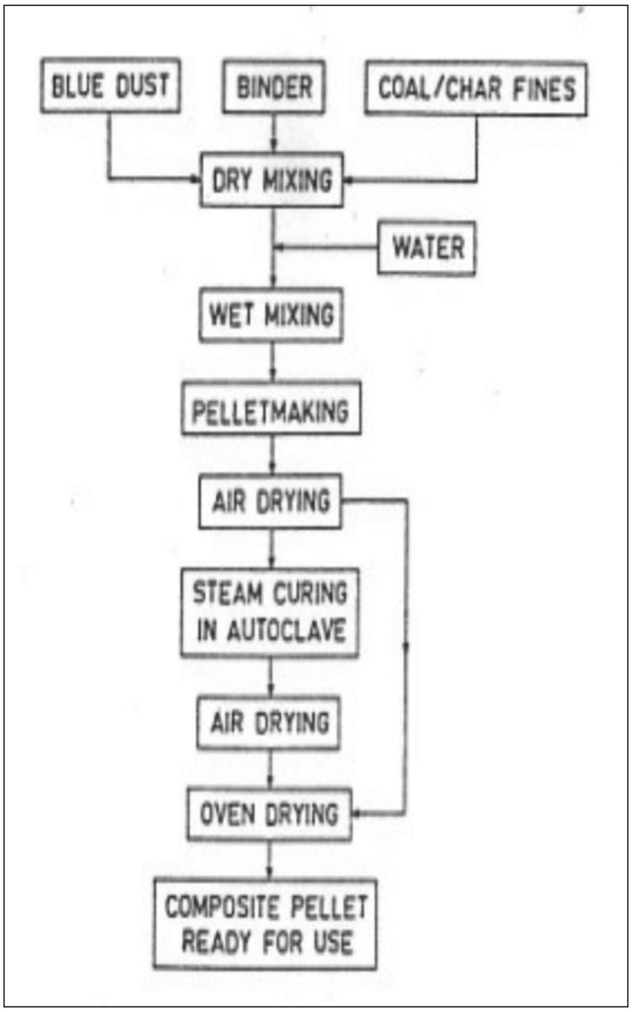

Fig. 1 : Flow diagram for composite pelletmaking

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The pellet-making procedure is shown in Fig. 1. For devolatilization studies, blue dust was replaced by inert alumina powder. Fig 2 shows the experimental apparatus. The cylindrical green pellets of coal – alumina powder mix was made in a die & punch assembly by once impacting the wet powder-mix. Various binders like organic, inorganic, and organic –inorganic mixture were employed.as. Diameter and height of dry pellets varied from 10.3 to 10.5 mm and 10.3 to 12.0 mm respectively. Compressive strength was measured by INSTRON. The paper by Dutta and Ghosh [3] has reported details of the pellet-strength.

Non-isothermal experiments were performed using the set-up for non-isothermal kinetic study, see Fig. 2. A Kanthal-wound vertical furnace 500 mm long was used for heating. The temperature of the hot zone of the furnace was controlled at 1273 K. The reaction chamber was a 15 mm I.D. and 420 mm long transparent fused-silica tube closed at the bottom. The reaction chamber containing the pellet sample was lowered into the hot zone of furnace by a stepper motor assembly and a slow flow of purified argon was maintained. Initial and final weights of samples were noted separately. Several samples of exit gas were taken for gas chromatographic (GC) analysis during each experiment.

Non-Isothermal Devolatilization of Coal – General Features

Experimental details for study of devolatilization of coal were:

1. Coal type : 2 (Hutar, Bachra, low pct. ash)
2. Downward speed of reaction chamber : 2 (0.124 and 0.062 mms-1)
3. Maximum temperature : 1 (1273 K)
4. Carrier gas in GC : 1 (Ar)

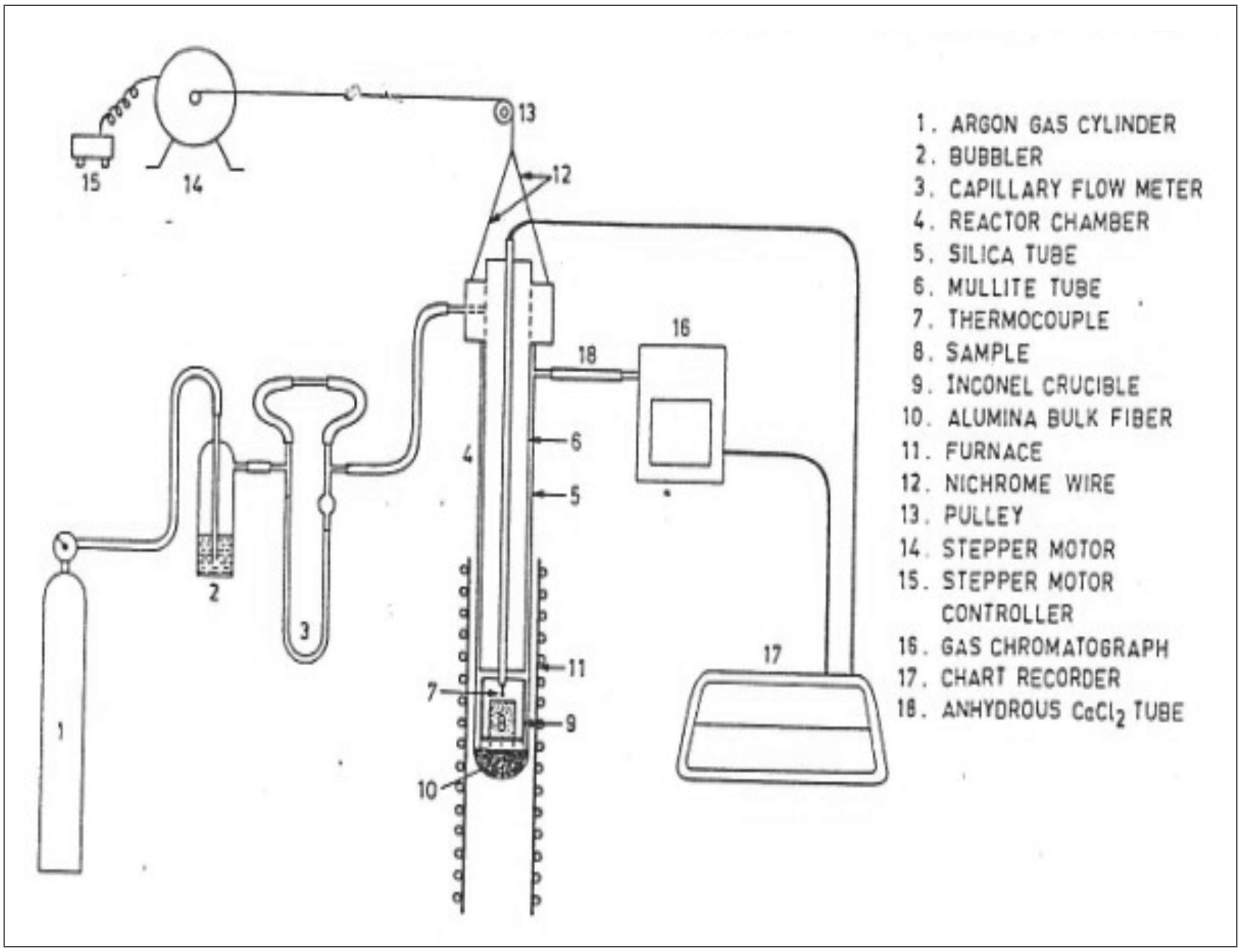


Fig. 2 : Set–up for non-isothermal kinetic studies

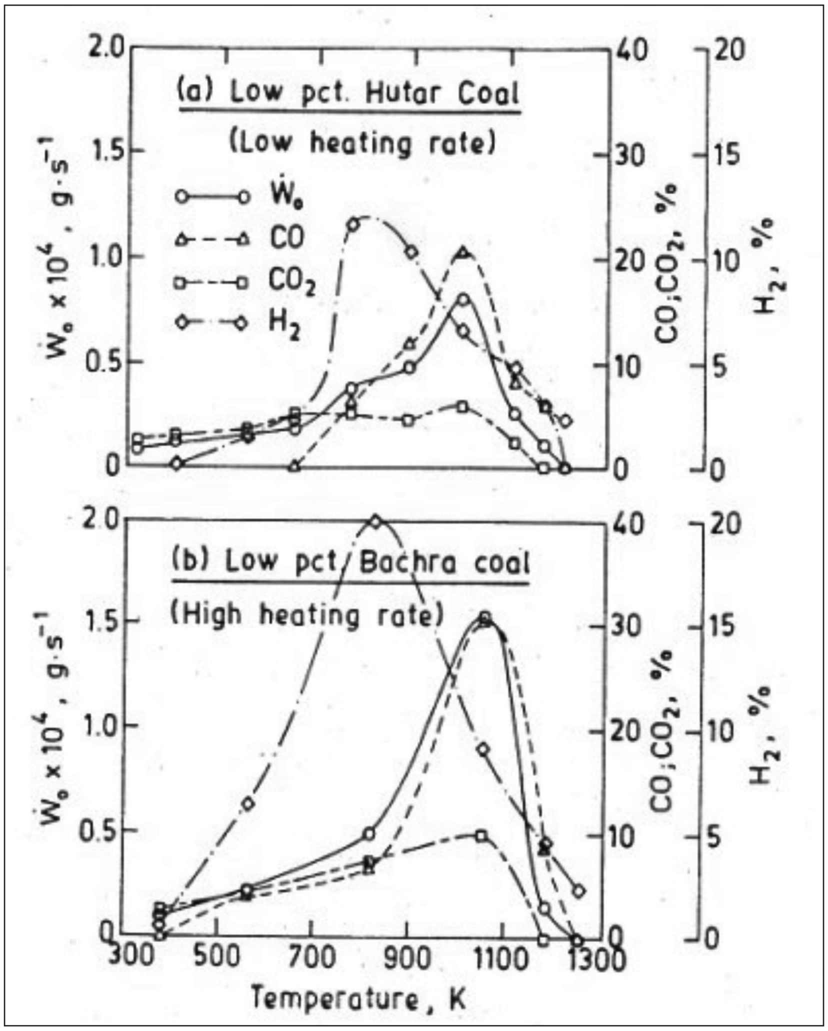


Fig . 3 : Variation of exit gas composition and W^xO with temperature for non –isothermal devolatilization studies of low pct. Bachra coal

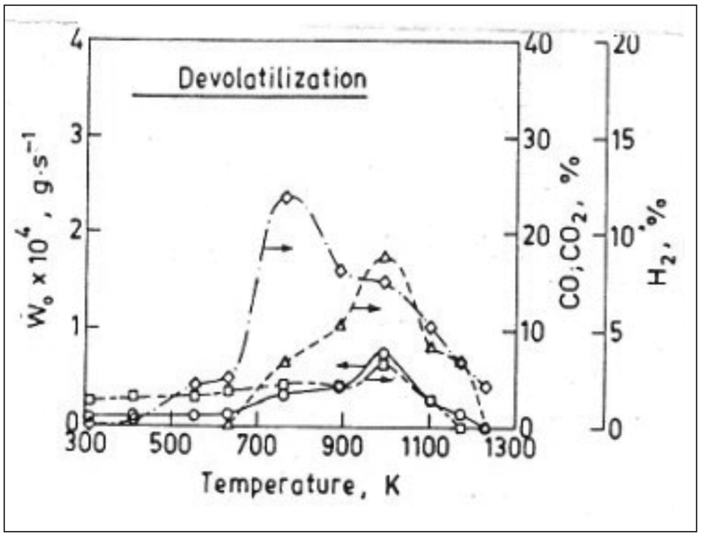


Fig. 4 : Variation of exit gas composition and W^xO with temperature for non–isothermal devolatilization studies of low pct. Hutar coal at high heating rate.

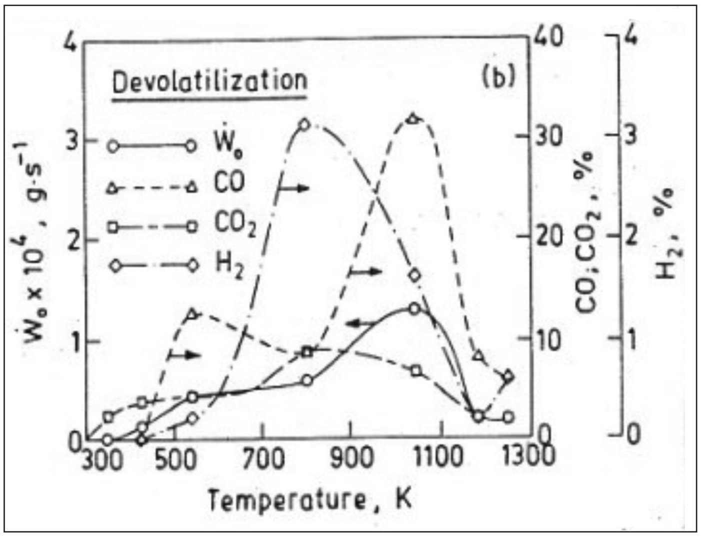


Fig. 5 : Variation of exit gas composition and W^xO with temperature for non –isothermal devolatilization studies of low pct. Bachra coal at low heating rate

Figures 3, 4 and 5 show gas chromatographic data for devolatilization of Hutar and Bachra coal. The % compositions of various gaseous species as well as rate of oxygen loss (W^xO) due to evolution of CO and CO_2 have been presented. These have been plotted as function of temperature for better understanding of the phenomenon.

Hydrocarbons decompose at high temperatures by cracking, as higher HC's convert to lower HC's along with Carbon (1).

Gasification of carbon by CO_2 and steam takes place as follows :

$C (s) + CO_2 (g) = 2 CO (g)$ (2)

$C (s) + H_2O (g) = CO (g) + H_2 (g)$ (3)

Rate of oxygen loss (W^xO) = $2W^xCO_2 + W^xCO$ (4)

where W^xCO_2 and W^xCO are the rates of evolution of CO_2 and CO respectively in gms^{-1}.

A number of books [6,7] comprehensively cover the subject of coal, while a recent review on chemistry of coal [8] is also worth noting. Some points from these references follow:

A series of consecutive and parallel reactions occur during pyrolysis of coal. Although most if the free water is driven off below 373 K, the combined water is not removed until the temperature reaches around 575 K. Significant devolatilization does not start until 625 to 675 K is reached.

There are two stages of devolatilization of coal, namely primary (at 625 to 875 K) and secondary (above 875 K). Coal undergoes a series of complex physical and chemical changes upon heating, which causes thermal rupture of bonds, while volatile constituents escape from the coal. The variety of products include H_2O, CO_2, CO, C_2H_6, CH_4, tar + liquid, H_2 etc.

Kinetics of Devolatilization

The general rate equation for devolatilization may be written as :

$$dx / dt = k_n (a - x) n \qquad (5)$$

where x is a dimensionless kinetic parameter $\Delta V / \Delta V_0$, where ΔV is the volatile matter content of coal and ΔV_0 is the total volatile matter of raw coal, t is time, kn is nth order rate constant , and a is a dimensionless kinetic parameter .

Solving for the second order gives the following :

$$1 / (a-x) = 1 / (a - x_i) + k_2 t \qquad (6)$$

where $x = x_i$ at $t = 0$.

Similarly the following equation is obtained for the first order reaction :

$$\ln [(a- x_i) / (a - x)] = k_1 t \qquad (7)$$

For the zeroth order, the equation (5) reduces to :

$$x = x_i + k_0 t \qquad (8)$$

The overall pyrolysis process above 673 K may be described by an initial second order decomposition-reaction followed by a first order diffusion-process in which the escape of the products of decomposition through the pores is rate-determining.

Oxygen and Hydrogen Balance for Devolatilization

Tables 1(a) and 1(b) record the results of oxygen and hydrogen balance for non – isothermal devolatilization experiments [1, 2, 4].

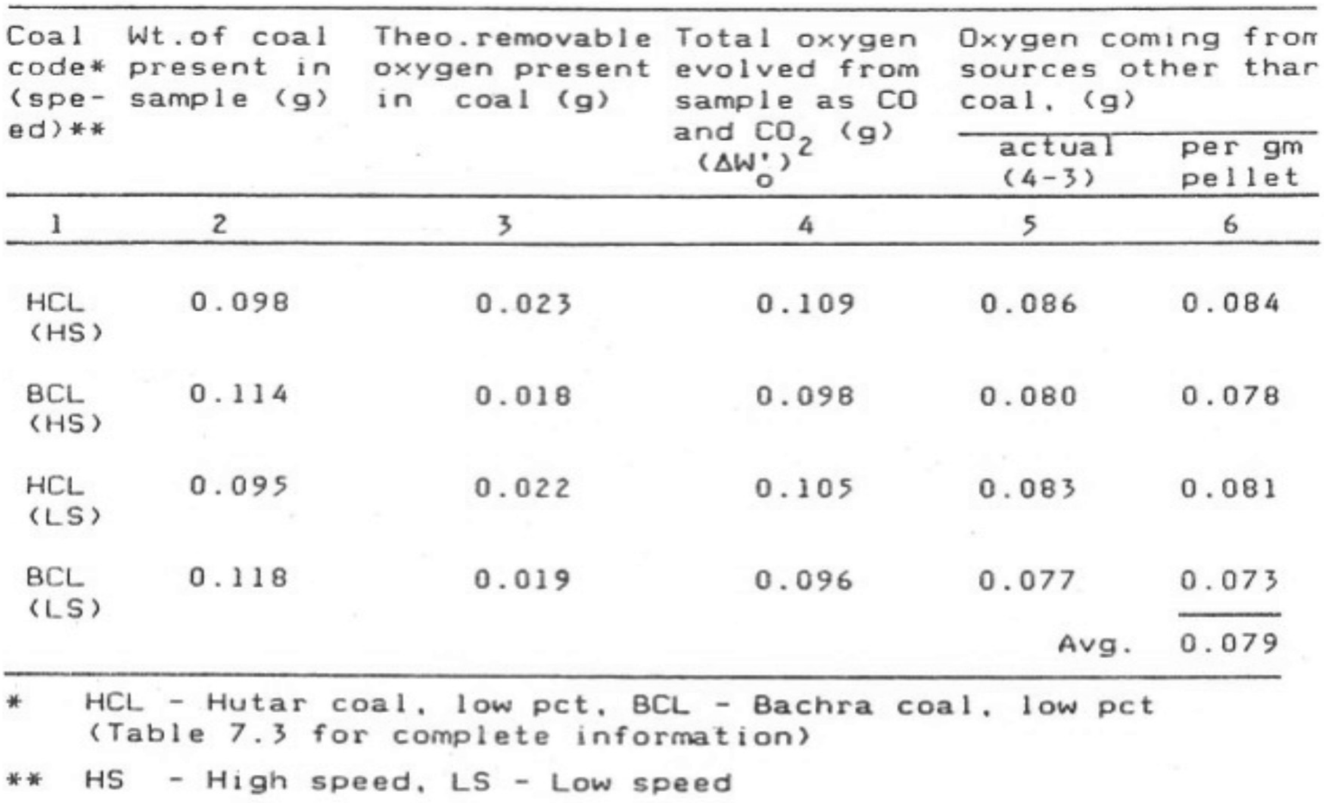
The oxygen contents (with organic matters) of Hutar and Bachra coals are 23.5 and 15.9 wt. %respectively. Since this oxygen gets removed with volatiles and gases during devolatililization, these provide the values of theoretical removable oxygen in the coal [Column 3, Table 1(a)].

Total oxygen loss associated with evolution of CO and CO_2 ($\Delta W^x O$) was calculated by graphical integration of $W^x O$ as function of temperature from Figs 3, 4 and 5. These values are shown in Column 4 of Table 1 (a). An interesting observation is that $\Delta W^x O$ is much larger than the theoretical oxygen content of coal. Table 1 (b) also shows the mass of additional oxygen generated from moisture, which is 8 times the mass of additional hydrogen, as expected. The moisture content in exit gas was 2% maximum. Though other hydrocarbons could not be detected by gas chromatography, most of them were higher ones and got condensed in the exit tubes of the reaction chamber during the experiments.

Coals from the Jharia mines, Dhanbad and Bhilai Steel Plant were ground to – 100 mesh and a study by Sha and Dutta [4] showed significant removal of free moisture from such coals below 375 K, but complete moisture removal required 575 K. Pattison et al [5] studied non-isothermal pyrolysis of coal in the range of 298 to 1123 K in an inert atmosphere. Exit gas analysis by gas chromatography revealed presence of C_2H_4, C_2H_2, CO_2, CH_4, CO, H_2.

Table 1(a)

Oxygen Balance Calculation for Devolatilization Experiments

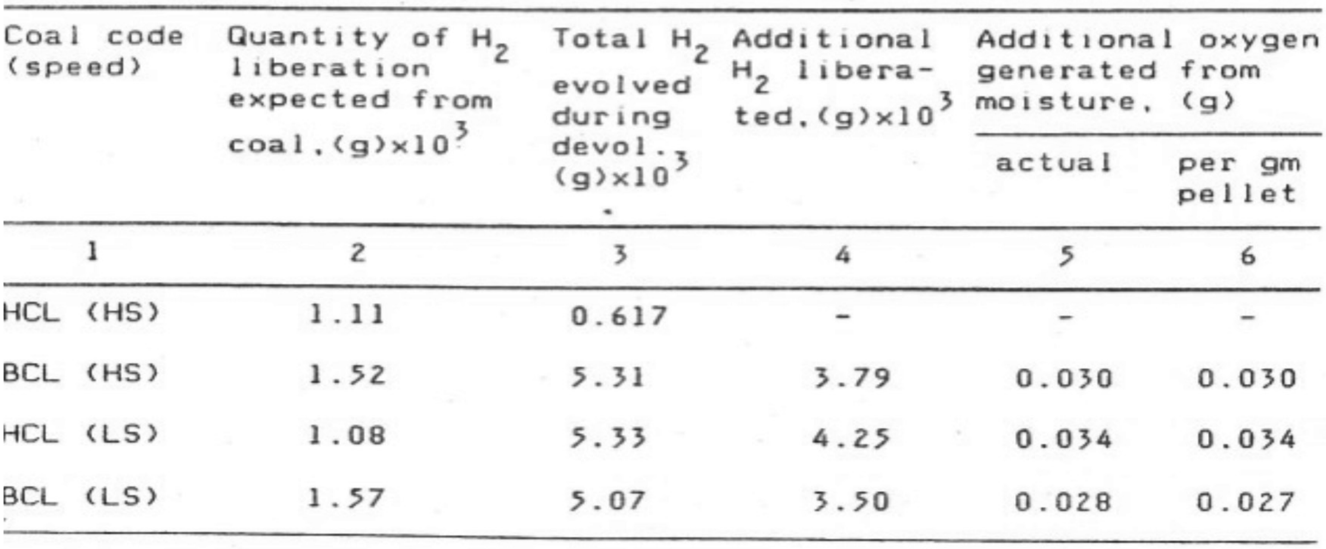


Coal code* (speed)**	Wt.of coal present in sample (g)	Theo.removable oxygen present in coal (g)	Total oxygen evolved from sample as CO and CO_2 (g) $(\Delta W'_o)$	Oxygen coming from sources other than coal, (g)	
				actual (4-3)	per gm pellet
1	2	3	4	5	6
HCL (HS)	0.098	0.023	0.109	0.086	0.084
BCL (HS)	0.114	0.018	0.098	0.080	0.078
HCL (LS)	0.095	0.022	0.105	0.083	0.081
BCL (LS)	0.118	0.019	0.096	0.077	0.073
				Avg.	0.079

* HCL - Hutar coal, low pct, BCL - Bachra coal, low pct (Table 7.3 for complete information)

** HS - High speed, LS - Low speed

Table 1(b)
Hydrogen Balance Calculation for Devolatilization Experiments



Coal code (speed)	Quantity of H_2 liberation expected from coal, (g)x10^3	Total H_2 evolved during devol. (g)x10^3	Additional H_2 liberated, (g)x10^3	Additional oxygen generated from moisture, (g)	
				actual	per gm pellet
1	2	3	4	5	6
HCL (HS)	1.11	0.617	-	-	-
BCL (HS)	1.52	5.31	3.79	0.030	0.030
HCL (LS)	1.08	5.33	4.25	0.034	0.034
BCL (LS)	1.57	5.07	3.50	0.028	0.027

Concluding Remarks

The present paper is provides a gist of some of the important studies on non-isothermal devolatilization of coal, but excludes the large-bed devolatilization of higher HCs and the contents of this note have direct relevance to the industrial coke oven practices.

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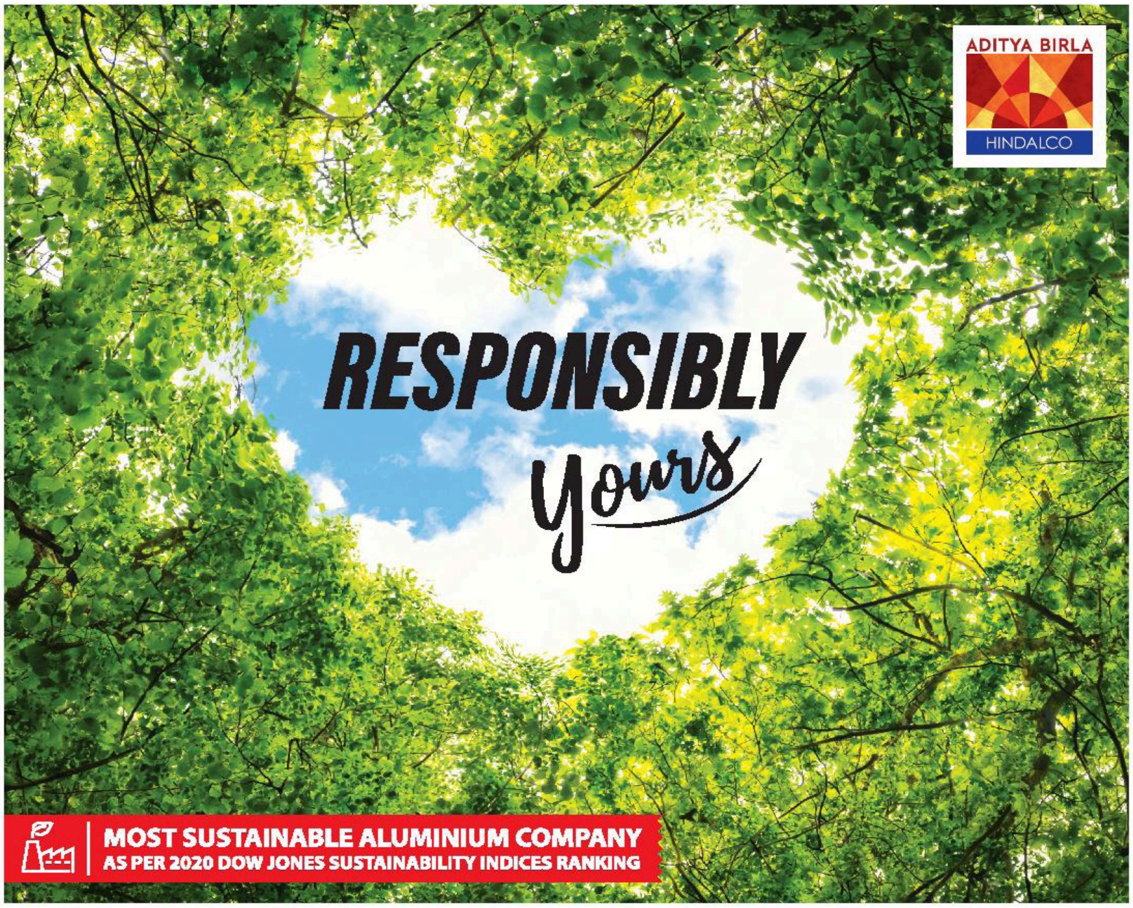
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IIM's Former President's Interview to The University of Illinois

by Emily Jankauski

Our alumni are leaders of industry. Sanak Mishra, former president of the Indian National Academy of Engineering, is one of our stand-out University of Illinois Urbana-Champaign's Materials Science and Engineering alumni.

Mishra earned a master's in 1970 from UIUC followed by a doctorate in 1973. He became the founding member of the Research & Development Centre for Iron & Steel at Ranchi, a corporate unit of the Steel Authority of India Limited. In his 25-year stint at SAIL he worked his way up to managing director of its large integrated steel plant at Rourkela.

Mishra climbed his way up the ladder becoming group vice president and CEO of India Projects of ArcelorMittal, the world's largest steelmaker. He went on to become the first secretary general of the Indian Steel Association, where he helped establish India's National Steel Policy and set up the Steel Research and Technology Mission of India.

In 2010, he was recognized with the Distinguished Merit Alumni Award. Mishra also authored an autobiography, "Sanak Mishra: An Autobiography," in 2020 detailing his prolific scientific accomplishments and career.

Let's chat with our all-star alumnus in a Q&A!

Q: What made you interested in materials science and engineering?

A: "Before coming to UIUC as a graduate student in 1968, I had done a bachelor of engineering degree in metallurgy at the Indian Institute of Science, Bangalore. I had pursued this after obtaining an undergraduate honors degree in physics, with chemistry and mathematics as additional subjects.

"On both occasions I came to understand that exciting new developments were taking place in an interdisciplinary field that was being referred to as materials science and engineering. It is the interdisciplinary nature of the subject field that held my fascination and interest. I also thought I had the right academic background to pursue it."

Q: Why did you choose MatSE at Illinois for graduate school?

A: "I had found out that the University of Illinois at Urbana-Champaign was not only one of the top universities in the world in the field of engineering and solid-state physics, (but) its graduate school of metallurgy, as it was then called, had a world-wide reputation as well. I was particularly interested in the physics of metals and how it exerted a strong bearing on the magnetic, electrical, electronic and mechanical properties of all materials. UIUC was a clear leader in the domain."

Sanak Mishra, front row, second from left, is all smiles with his thesis advisor professor Paul Beck, first row, left, and laboratory-mates in front of the Materials Science and Engineering building on Green Street in Urbana, Ill. in 1969

Q: What are some of your fondest memories from your time at MatSE at Illinois?

A: "Professor Paul Beck, one of the greatest names in physical metallurgy, was my thesis advisor for (my) master's and doctorate. I had the fortune of working with him as his research assistant for five straight years. Besides being a brilliant mind, he was (also) passionate about the research programs he had initiated. I was inspired by him and enjoyed working with him. I learned much from him, among other things the virtues of work ethics.

"Professor Charles Wert was the chairman of the department. He was a kind and supportive human being (and was) highly respected for his scientific accomplishments. I had the opportunity to take courses from professors Ted Rowland, Marvin Metzger and Howard Birnbaum, who were all famous in their own right. The weekly colloquium, delivered by eminent scholars from all over the world, opened my eyes to the most recent advances in materials engineering."

Q: What kind of research did you conduct during your time as at Illinois?

A: "My research work at MatSE was on the nature and features of magnetism in alloys of transition metal elements. My experimental measurements went down to temperatures at and below liquid helium. We also collaborated with Simon Foner at the National Magnet Laboratory at MIT for certain measurements at high magnetic fields.

"My work with professor Beck led to establishing the presence of atomic, short-range order and magnetic clusters in dilute alloys of copper-iron and copper-nickel-iron. Because of the fundamental nature of the work and the significance of the results, we published several papers in physics journals."

Q: What kind of research do you conduct now?

A: "Coming back to India from UIUC in 1973, I joined as a founder member of the Research & Development Centre for Iron & Steel at Ranchi, which had just been established as a corporate unit of the Steel Authority of India Limited, the country's largest steel company.

"For the next 25 years, I was engaged in product and process innovations relating to steel. I may mention that in the year 1985, I delivered a symposium lecture (at) UIUC on my work on crystallographic textures in grain-oriented silicon steels. It was a proud moment for me as I was introduced by professor Beck, and professor Wert gave the concluding remarks. At RDCIS, along with my colleagues, I was able to take several patents. I received the National Metallurgist Award in 2003.

"Eventually, my career took a turn from research to technology planning and corporate strategy. My last stint (at) SAIL was as managing director of its large integrated steel plant at Rourkela. Subsequently I worked as (the) group vice president and CEO of India Projects of

Sanak Mishra poses with the senior bench, which was originally located by University Hall and now sits ourside the Illini Union. The bench was donated by the class of 1900.

ArcelorMittal, the world's largest steelmaker. My last fulltime engagement was as the first secretary general of the Indian Steel Association, where I worked closely with the government of India in the formulation of the National Steel Policy and in setting up the Steel Research and Technology Mission of India.

"In 2018, I received the Lifetime Achievement Award from the Ministry of Steel. In 2019 and 2020, I served as the president of the Indian National Academy of Engineering when I interacted with the government of India on matters of science and technology policy. Currently I am focusing on future prospects of us(ing) green hydrogen for production of green steel."

Q: How did your time at MatSE at Illinois prepare you for your career?

A: "MatSE gave me a strong foundation in the frontlines of science and in research methodology and structured learning techniques. It trained me in the art of pursuing an end result of meaningful and impactful value while being conscious of the larger picture. It also boosted my confidence in handling matters outside the realm of metals and materials. During 2015 and '16, I had the privilege of serving as the president of the University of Illinois Alumni Club in New Delhi.

Q: What advice do you have for current MatSE at Illinois students?

A: "Set for yourself a purposeful goal that explores the unknown. Work hard and with passion to achieve it."

Q: What do you cherish most about your time at the U of I?

A: "This is where I met my future wife Veena Paralkar, hailing from Bombay, who was also a graduate student there. I might add that she received two master's degrees at UIUC — one in library science and a second one in journalism and communication. After working for three years at City University of New York, upon our return to India she took up a successful career in information and documentation and corporate communication."

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RECENT DEVELOPMENTS

World's first 3D-printed steel bridge opens to public in Amsterdam

World's first 3D-printed steel bridge was opened to the public in Amsterdam earlier this month. It was developed by MX3D, a Dutch robotics company, in collaboration with a consortium of experts, and represents a major milestone for 3D-printing technology.

After four years in development, the bridge was unveiled by Her Majesty Queen Máxima of the Netherlands. It was installed over one of the oldest canals in Amsterdam's city centre – the Oudezijds Achterburgwal.

The 12-metre-long steel structure will be a 'living laboratory' that will capture and transmit data on its health in real-time to show how it changes over its lifespan. The smart sensor network was designed and installed by a team from The Alan Turing Institute.

The sensors attached to the structure will gather data on air quality, temperature, strain, displacement and vibration. The data will be used by the bridge's 'digital twin', a computer model that will emulate the actual bridge in real-time, to improve accuracy over time. The computer model will help understand how a full-scale 3D-printed steel structure works in real-world.

Her Majesty Queen Máxima of the Netherlands unveiled the bridge. | Photo Credit: MX3D

"3D printing is poised to become a major technology in engineering, and we need to develop appropriate approaches for testing and monitoring to realise its full potential," Mark Girolami, Professor at The Alan Turing Institute, said in a release. "When we couple 3D printing with digital twin technology, we can then accelerate the infrastructure design process, ensuring that we design optimal and efficient structures with respect to environmental impact, architectural freedom and manufacturing costs."

Source : The Hindu

ArcelorMittal Nippon Steel India to invest Rs 1,66,000 crore in Gujarat

The Gujarat government said ArcelorMittal Nippon Steel India (AMNS India), which owns a steel mill at Hazira in Surat, will invest Rs 1,66,000 crore in six different projects in the state. A memorandum of understanding (MoU) for this proposed investment was signed by Additional Chief Secretary (Industries and Mines) Rajiv Kumar Gupta on behalf of the Gujarat government, and by AMNS India CEO Dilip Oommen, said the state government in a statement. The MoU was signed in the presence of Gujarat Chief Minister Bhupendra Patel in Gandhinagar.

According to the pact signed by both parties, the steel giant will invest Rs 4,200 crore for the expansion and modernisation of their captive jetty in Hazira and Rs 45,000 crore to increase the Hazira plant's steel production capacity from the current 8.6 MMtpa to 18 MMtpa, said the statement.

The company will invest Rs 30,000 crore to expand their facility at Suvali in Surat and Rs 30,000 crore to develop Surat steel city and industrial cluster at Kidiabet in Surat, said the statement. Moreover, the company will invest Rs 40,000 crore to set up solar, wind and hybrid power generation facilities across the state having a cumulative capacity of generating 10 gigawatts of clean energy, according to the statement.

The first such renewable energy plant of the 2,200-megawatt (MW) capacity will come up at the Kana Talav area of the Bhavnagar district, said the statement, adding that a separate MoU for this project was also signed. In addition, the company will pump in Rs 17,000 crore in a "downstream coke oven" project at Hazira in Surat, said the statement.

In all, the company will invest Rs 1,66,000 crore in six projects, which will generate nearly 1.80 lakh direct as well as indirect employment opportunities, said the statement.

The Economic Times

Adani Group signs MoU with South Korean steelmaker POSCO to set up an integrated steel mill

Indian conglomerate Adani Group will be joining hands with the Korean steel company, Posco to develop and establish an integrated steel mill in Mundra, Gujarat with a planned investment of $5 billion (approx. Rs 37,000 crore)

“We are very pleased to announce the partnership with POSCO, the world’s most efficient and advanced steel manufacturer, in steel production and carbon reduction,” said Gautam Adani, Chairman of the Adani Group in a media statement.

The non-binding MoU signed between POSCO and Adani intends to further collaborate at the group business level in various industries such as renewable energy, hydrogen, and logistics in response to carbon reduction requirements, the company’s statement said. Both parties are examining various options to cooperate and leverage the technical, financial, and operational strengths of each company.

The collaboration includes evaluating a joint Integrated Steel Mill at Mundra, Gujarat, based on POSCO’s technology and R&D capability.

“POSCO and Adani intend to utilize renewable energy resources and green hydrogen, in line with both partners’ ESG commitments to sustainability and energy efficiency,” the company’s statement said.

The Economic Times

JSW Steel says group’s combined output grows 28% to over 5 Mt in Oct-Dec

JSW Steel posted a 28 per cent year-on-year growth in group combined steel production at 5.35 Mt during the quarter ended December 30, 2021.

In a statement, the JSW Group company said it had produced 4.18 Mt in the October-December period of the financial year 2020-21. “JSW Steel reported group’s combined crude steel production at 5.35 Mt for Q3 FY22, including the production at jointly controlled entity viz. JSW Ispat Special Products Ltd (JISPL)," it said.

JSW Steel's standalone output rose by 8 per cent to 4.41 Mt from 4.08 Mt in the year-ago quarter, the statement said. The capacity utilisation of existing operations at standalone level was at 94 per cent during the third quarter of the ongoing 2021-22 financial year. JSW Steel is the flagship business of the diversified USD 13 billion JSW Group.

JSW Group has other business interests also in sectors such as energy, infrastructure, cement, paints, sports and venture capital.

The Economic Times

Tata Steel reports a 16% jump in crude steel production for 9 months of FY22

Tata Steel Ltd's crude steel production grew by 16% year-on-year (yoy) to 14.16 Mt as at the end of nine months ending 31st December 2021, and its total deliveries increased by 4% at 13 Mt yoy on the back of continued economic recovery.

"During the third quarter of FY22, Crude steel production was up 1.5% quarter-on-quarter (qoq) to 4.8 Mt and overall deliveries were lower by 4% (qoq) 4.41 as an increase in domestic deliveries was offset by lower exports," the company said in a statement.

Tata Steel's Automotive & Special Products segment deliveries increased by 53% yoy in 9 months ending FY22 and the 3QFY22 deliveries were broadly similar on QoQ basis, the company said. Branded Products & Retail segment deliveries increased by around 14% yoy in 9 months FY22 with 3QFY22 deliveries were higher by 2% qoq.

"Tata Steel's micro-segmentation approach in the MSME segment has helped to increase the downstream branded play by 31%," the company's statement said.

Industrial Products & Projects segment deliveries increased by 11% yoy in 9 months FY22; 3Q FY22 deliveries were higher by 3% qoq with an increased focus on value-added products, the company said.

The Economic Times

JSW Steel to invest Rs 15,000 crore to expand Vijayanagar facility to 18 Mtpa by FY 24

JSW Steel announced a 15,000-crore brownfield expansion project at its Vijaynagar Steel Works to increase capacity by 5 Mt per annum by FY 24.

"This expansion reiterates our commitment to be a significant partner in building a stronger India through sustainable means," said JSW Group's chairman, Sajjan Jindal in a media statement.

JSW said that it has received the environmental clearance for the project and is planning to complete 1 Mtpa expansion through upgradation of the current facility to achieve 13 Mtpa capacity within the next 12 months.

The company aims to take its Vijayanagar facility 18 Mtpa by FY24.

"We will create new job opportunities as well as generate immense value for all our stakeholders. Through the introduction of Artificial Intelligence and other Industry 4.0 interventions at this facility, it will become an integral part of our network of digitally connected smart steel factories in India," Jindal said.

The Economic Times

Lithium price surge could charge demand for lead in batteries

Lead demand may get a boost in 2022 as battery makers opt for cheaper alternatives to lithium, Chinese research house Antaike said. Lead-acid batteries are commonly used in internal combustion engine cars and have steadily lost ground to lithium-ion batteries favoured in the burgeoning electric vehicle (EV) sector.

"The price of lead in the second half of this year was very much stabilised, but for lithium it was picking up very fast," Antaike analyst Zhang Zhiwei told the China Lead and Zinc Conference. Prices for battery-grade lithium carbonate in China have more than quadrupled this year to a record high of 232,500 yuan ($36,514) per tonne on resurgent EV demand.

https://auto.economictimes.indiatimes.com/

Rourkela - Student Affiliate Chapter

IIM Rourkela Student Affiliate Chapter organised the Distinguished Lecture on "Multicomponent High-Entropy Cantor Alloys" on 13th December 2021 at 05:30 pm (IST). The lecture was delivered by Prof. Brian Cantor, Department of Materials, Oxford University, BCAST, Brunel University.

The lecture includes several aspects related with the development of High entropy alloys The webinar concluded with the vote of thanks by Prof. Anindya Basu (HOD, Metallurgical and Materials Engineering, NIT Rourkela) (Faculty Advisor, Indian Institute of Metals Student Affiliate Chapter). The lecture was live streamed on YouTube and total views were around 190.

Visakhapatnam Chapter

The webinar on "Fundamental and Practical Aspects of Dephosphorisation in Basic Oxygen Furnace (BOF) Steel Making Process" was organised by the IIM Visakhapatnam Chapter on 23rd December 2021. The speaker was Dr. Ajay Kumar Shukla, Associate Professor, Department of Metallurgical and Materials Engineering, IIT-Madras.

The session was inaugurated by Sri Abhijeet Chakrabarty, CGM (Works) I/c. In his address, he shared steel making process at Vizag Steel in brief and wished for valuable interaction with Dr Shukla and steel making professional. He complemented IIM chapter for inviting large number of Under and Post Graduate Metallurgical Students for this session as they will be immensely benefited on the given topic. While addressing to large number Steel Melt Shop, Vizag Steel Engineer attending this webinar, he made appeal for having detailed interactions on all the problem with guest faculty.

Dr. Shukla in his presentation covered both theoretical aspects and practical aspects on given topic. A number of case studies and findings were presented during this session and new approach of De-phosphorization techniques and related processes were covered. A number of queries rose during this session from Steel Makers and Students were well addressed by Guest Faculty.

The webinar was coordinated by Hon Secretary, Joint Hon Secretaries, Hon Treasurer of IIM, Visakhapatnam Chapter under the able guidance of Chapter Chairman Sri K K Ghosh.

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ADVERTISERS' INDEX

Name of the Organisations	*Page Nos.*
Chennai Metco Pvt Ltd	**2nd Cover**
Pragati Defence Systems Pvt Ltd	**5**
PTC Industries Limited	**25**
Tata Steel Ltd	**26**
Hindalco Industries Ltd	**27**
JSW Steel Ltd	**4th Cover**

OBITUARY

With deep anguish and sadness we would like to convey that the veteran global steel industry leader Mr. Malay Mukherjee passed away on January 29, 2022. He was the Honorary Member of IIM since 2007.

Mr. Mukherjee had over 43 years of experience in a range of technical, commercial and managerial roles in the mining and steel industry. He acquired Bachelor of Science degree from Indian Institute of Technology Kharagpur and Master's degree in mining from the USSR State Commission in Moscow. He served as Executive Director of Works at the Bhilai Steel Plant at Steel Authority of India Limited between 1991 and 1992. He joined Ispat International in 1993 and served as Executive Director for Mexico until 1995, Managing Director Mexico between 1995 and 1996 and General Director for Ispat Kazakhstan between 1996 and 1999. He later went on to serve as the CEO of Ispat Europe between 1999 and 2000. He served as President and Chief Operating Officer of Ispat International London between 2002 and 2004. He also served as the COO for Mittal Steel Company between 2004 and 2006. After merger with Arcelor, he served as the Senior Executive Vice President at ArcelorMittal between 2006 and 2008 and a Member of the Group Management Board, in charge of mines and steel plant operations in Africa, Asia, southern Europe (Bosnia, Macedonia), CIS, Ukraine, Kazakhstan and responsible for ArcelorMittal Group Business segments of Stainless Steel, Pipes, Tubes and Technology in Asia, CIS and South Africa. Later, Mr. Mukherjee served as the CEO of the ESSAR Steel Global during October 2009 and 2011. Currently, Mr. Mukherjee was Chairman for VA Tech Wabag Ltd. He was also on the board of Petropavlovsk Plc, JSW Steel Ltd and Uttam Value Steels Ltd.

May his soul rest in peace eternally.

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STEEL STATISTICS

World crude steel production for the 64 countries reporting to the World Steel Association (worldsteel) was 155.0 million tonnes (Mt) in January 2022, a 6.1% decrease compared to January 2021.

Crude steel production by region

Africa produced 1.2 Mt in January 2022, up 3.3% on January 2021. Asia and Oceania produced 111.7 Mt, down 8.2%. The CIS produced 9.0 Mt, up 2.1%. The EU (27) produced 11.5 Mt, down 6.8%. Europe, Other produced 4.1 Mt, down 4.7%. The Middle East produced 3.9 Mt, up 16.1%, North America produced 10.0 Mt, up 2.5%. South America produced 3.7 Mt, down 3.3%.

- Africa: Egypt, Libya, South Africa
- Asia and Oceania: Australia, China, India, Japan, New Zealand, Pakistan, South Korea, Taiwan (China), Vietnam
- CIS: Belarus, Kazakhstan, Moldova, Russia, Ukraine, Uzbekistan
- European Union (27)
- Europe, Other: Bosnia-Herzegovina, Macedonia, Norway, Serbia, Turkey, United Kingdom
- Middle East: Iran, Qatar, Saudi Arabia, United Arab Emirates
- North America: Canada, Cuba, El Salvador, Guatemala, Mexico, United States
- South America: Argentina, Brazil, Chile, Colombia, Ecuador, Paraguay, Peru, Uruguay, Venezuela

Top 10 steel-producing countries

	Jan 2022 (Mt)	% change Jan 22/21
China	81.7 e	-11.2
India	10.8	4.7
Japan	7.8	-2.1
United States	7.3	4.2
Russia	6.6 e	3.3
South Korea	6.0 e	-1.0
Germany	3.3	-1.4
Turkey	3.2	-7.8
Brazil	2.9	-4.8
Iran	2.8 e	20.3

e - estimated. Ranking of top 10 producing countries is based on year-to-date aggregate

Source : worldsteel.org

Total Production of Crude Steel in Last 5 Years

(million tonnes)

Country		2017	2018	2019	2020	2021
World		1735.1	1826.6	1875.3	1880.4	1951.9
1	China	870.7	929.0	995.4	1064.7	1032.8
2	India	101.5	109.3	111.4	100.3	118.2
3	Japan	104.7	104.3	99.3	83.2	96.3
4	United States	81.6	86.6	87.8	72.7	85.8
5	Russia	70.5	72.1	71.7	71.6	75.6
6	South Korea	71.0	72.5	71.4	67.1	70.4
7	Turkey	37.5	37.3	33.7	35.8	40.4
8	Germany	43.3	42.4	39.6	35.7	41.0
9	Brazil	34.8	35.4	32.6	31.4	36.2
10	Iran	21.2	24.5	25.6	29.0	28.5
11	Italy	24.0	24.5	23.2	20.4	24.4
12	Taiwan, China	22.4	23.2	22.0	21.0	23.2
13	Vietnam	11.5	15.5	17.5	19.9	23.0
14	Ukraine	21.4	21.1	20.9	20.6	21.4
15	Mexico	19.9	20.2	18.4	16.8	18.5
16	Indonesia	5.2	6.2	8.6	12.9	14.3
17	Spain	14.4	14.3	13.6	11.0	14.2
18	France	15.5	15.4	14.5	11.6	13.9
19	Canada	13.2	13.4	12.9	11.0	13.0
20	Egypt	6.9	7.8	7.3	8.2	10.3

Source : WSA