

A brief history of alloys and the birth of high-entropy alloys



1.1 Introduction

Alloying is the greatest gift of metallurgy to humankind. The English insists on unalloyed pleasures, thereby implying that the sensation of pleasure must be pure and not admixed with other emotions, exactly the opposite rules in metallurgy, where pure metals have few uses but lot more upon alloying. The power of this idea of alloying is not confined to metals. The same principle of alloying applies in polymers and ceramics. It can be carried further by mixing two classes of materials to create a variety of composites.

The civilizational journey of the society began with the discovery of native metals such as gold and copper as pure metals. Nowadays, we have access to an incredible number and variety of materials. Ashby map (Ashby, 2011) shown in Fig. 1.1 gives a panoramic view of the development in the use of materials over 10 millennia. A graphic depiction of the different classes of materials from ceramics to metals, polymers, and more recently composites is vividly displayed. The passage from discovery through development to the design of materials can be noted. Ashby's (2011) map in terms of strength versus density shown in Fig. 1.2 demonstrates the filling of material-property space in a vivid fashion from 50,000 BCE up to the present scenario. In time-scale, the largest filling has occurred in the past 50 years during which envelopes of metals, ceramics, and composites had a large expansion, and new envelopes of synthetic polymers and foam materials take a significant space. But the filled area also seems to approach some fundamental limits beyond which it is difficult to go further (Ashby, 2011).

In many ways, the history of alloying is the history of metallurgy and materials science. Books and treatises have been written. An elegant and brief history is by Ashby (2008). Cahn (2001) has offered a magisterial survey of "The Coming of Materials Science." Ranganathan (2003) wrote on alloyed pleasures—an ode to alloying. In the following sections, a few episodes in this epic journey are covered.

1.2 The coming of alloys

Native alloys such as tumbaga and electrum are alloys of gold-copper and gold-silver, respectively. When platinum was discovered in 1735, it was compared with silver. Also, mixtures of platinum metals are found to occur in nature. It is an early example of multicomponent high-entropy alloys (HEAs), since platinum is often found as alloys with the other platinum group metals and iron mostly.

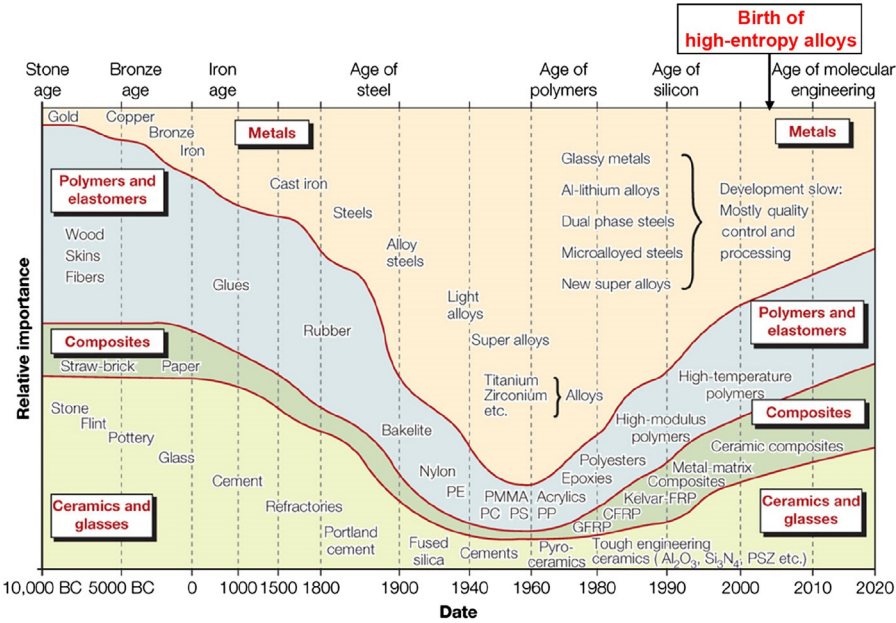


Fig. 1.1 Historical evolution of engineering materials marked with the birth of HEAs published in *Advanced Engineering Materials* (Yeh et al., 2004b). Adapted from Ashby M.F., 2011. *Materials Selection in Mechanical Design*, fourth ed., Butterworth-Heinemann, Elsevier, Oxford, UK.

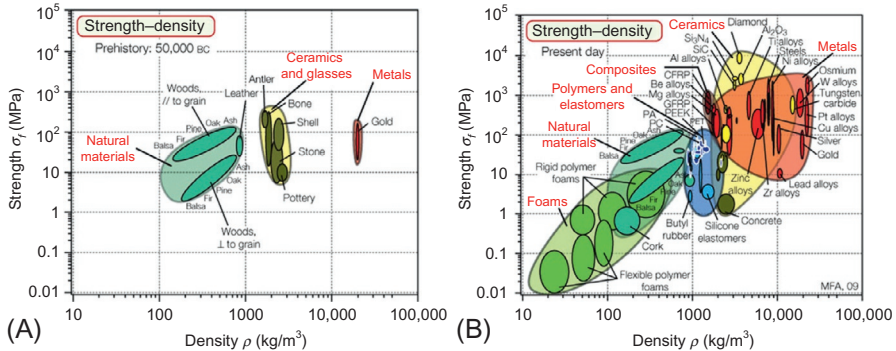


Fig. 1.2 The explosion in the diversity of materials in the modern era (Ashby, 2011): (A) prehistoric era (50,000 BCE) and (B) current status.

Alloying was an accidental discovery. In the primitive fires in the caves, ores of copper got mixed with ores of arsenic, zinc, and tin. The first alloy of copper and arsenic (arsenical bronze, 3000 BCE) was entirely accidental. A more intentional alloying of tin with copper (tin bronzes in 2500 BCE) gave birth to the Bronze Age, as bronze was superior in its mechanical properties.

The seven metals found in antiquity were gold, copper, silver, iron, lead, tin, and mercury. The eighth metal, zinc, is added not only because of the unique Indian context but also because the discovery of other metals had to await the advent of the scientific revolution for a few centuries.

It is interesting to mention that intermetallics of copper-tin alloys had been used in ancient time. Mirrors were made of bronzes in different parts of the Old World including India and China, due to their higher hardness, which makes it easy in getting mirror finish to reflect like silver. Archaeometallurgical investigations by Sharada Srinivasan on vessels from South Indian megaliths of the Nilgiris and Adichanallur (1000–500 BCE) showed that they were of wrought and quenched high-tin beta bronze, ranking among the earliest known artifacts. This is an early application of an intermetallic. When the sulfide ores of copper and nickel were smelted together, it led to copper-nickel alloy in the fourth century in China. Zinc was added in the 12th century to form silvery and rust-resisting alloy known as paktong (white copper), which was widely used in Europe before stainless steel was invented.

Wrought iron was produced as early as 1000 BCE, and cast iron and cast steel were produced one millennium later. Steel was an accidental alloy of iron with carbon. This is all the more astonishing as carbon was not recognized as an element until recently. This accidental discovery also led to the production of wootz steel in India around 300 BCE. This has been rightly celebrated as the most advanced material of the ancient world, as this steel was used to fashion the Damascus swords. The deciphering of wootz steel by European scientists led to the correlation between structure and properties at first and subsequently between composition, processing, structure, and properties. Fig. 1.3 shows that materials hypertetrahedron that links the above four with modeling is necessary to understand the performance of wootz steel (Ranganathan and Srinivasan, 2006; Srinivasan and Ranganathan, 2014). The facets of the ultrahigh-carbon steels, Buchanan furnace, the Fe-C phase diagram, the microstructure of dendrites in the as-cast state and spheroidized cementite in the forged state, the superplastic elongation, and the damascene marks are emphasized for the strong interconnections among them. It can be regarded as a classic example of the material tetrahedron but including a fifth vertex of modeling (e.g., CALculation of PHase Diagrams (CALPHAD) method to calculate phase diagram) to make it a hypertetrahedron.

When the first industrial revolution began in later half of 18th century in England, more and more elements were found and produced by humankind. From these “new” elements, numerous metallic materials including engineering and advanced alloys have been developed. They were synthesized with different compositions and produced by various processing routes. Up to now, about 30 alloy systems, each system based on one principal metallic element, have been developed and used for a variety of products (Handbook Committee, 1990).

Several alloys of engineering importance have been developed. Michael Faraday created some of the first alloy steels in his efforts to reproduce the wootz steel from India and is hailed as the father of alloy steel. Al alloys were produced after the commercialization of Hall-Héroult process in the mid-1880s and underwent large progress in precipitation-hardenable alloys such as Al-Cu(Mg) and Al-Zn-Mg-(Cu) for light and strong airframes in the explosive expansion of the airplane industry during and

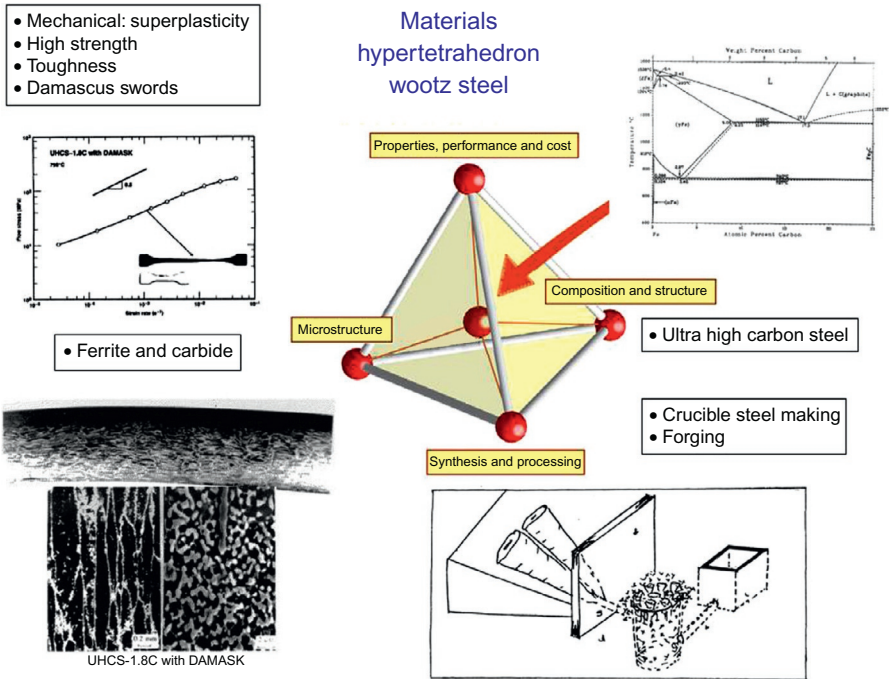


Fig. 1.3 The material hypertetrahedron for wootz steel.

From Srinivasan, S., Ranganathan, S., 2014. Indian's Legendary Wootz Steel-An Advanced Material of the Ancient World. Universities Press (India), Hyderabad, India.

after World War I (1914–1917). High-speed steel for cutting tools was first produced in the early 1900s. To meet the challenge for even higher cutting speed, cemented or sintered carbides of WC/Co composites were introduced in the 1930s. At the same time, superalloy development began in the United States in the 1930s and was accelerated by the demands of gas turbine technology. Ferritic, austenitic, and martensitic stainless steels were almost simultaneously developed around 1910.

1.3 Special alloys and composites

Besides the above modern engineering alloys, several special alloy systems with specific compositions, structures, and properties have been developed with intensive research in recent 50 years. They are intermetallics, quasicrystals, and metallic glasses as described in the following sections. In addition, this section also gives a brief introduction to composites.

1.3.1 Intermetallics and quasicrystals

Intermetallic compounds are basically compounds of two or more metallic elements. They are brittle by nature. Besides the ancient intermetallic mirrors made of high-tin bronze mentioned in the last section, they have given rise to various novel material

developments in modern time including magnetic AlNiCo alloys and the LaNi₅ for nickel-metal hydride batteries and various aluminides, Ni-Al-, Ti-Al-, and Fe-Al-based compounds, for elevated-temperature light-weight applications in turbine engines.

Another class of intermetallics includes those that demonstrate so-called forbidden rotational symmetries (such as 5- and 10-fold rotational symmetries) and quasiperiodic translational symmetry. These were discovered by [Shechtman et al. \(1984\)](#) in 1982 as described in his notebook, when he first observed a 10-fold electron diffraction pattern from a rapidly solidified Al-Mn alloy. These were christened as quasicrystals. This observation has shaken the beliefs of crystallographers to the extent that the definition of a crystal has been modified in 1990, based on the discovery of this new class of materials. There has been intensive research on these exciting materials in the past four decades, both toward the understanding of the structure and properties of these materials.

1.3.2 *Metallic glasses*

The first reported metallic glass was an alloy (Au₇₅Si₂₅) produced at California Institute of Technology by the research group of Pol Duwez ([Klement et al., 1960](#)), which was cooled rapidly from the liquid state at a rate of around 10⁶ K/s to avoid crystallization and possess noncrystalline or glass-like structure. Among the different metallic glasses developed later, the soft magnetic metallic glass of iron, nickel, phosphorus, and boron, known as Metglas, was commercialized in early 1980s and is used for low-loss power distribution transformers. In 1974, H.S. Chen first reported that bulk metallic glass rods in diameters ranging from 1 to 3 mm can be produced in various glassy ternary alloys including Pd-Au-Si, Pd-Ag-Si, and Pt-Ni-P systems ([Chen, 1974](#)). After this discovery, multicomponent glassy alloys based on lanthanum, magnesium, zirconium, palladium, iron, copper, titanium, etc. with critical cooling rate in the range of 1–100 K/s, comparable with oxide glasses, have been developed and researched.

1.3.3 *Composites*

Metals, ceramics, and polymers individually have a number of limitations, which have led to the development of composites, which are a combination of two or more of these combinations. Composites are usually classified based on the matrix of the composites. Accordingly, we have metal matrix composites, polymer matrix composites, and ceramic matrix composites, each of which has found a place in various applications, wherein metals, polymers, and ceramics have not been able to meet the requirements of such applications individually. Polymer matrix composites, particularly glass fiber-reinforced composites, are being used in a number of applications in transport industry including aerospace due to their lightness and high specific strength. Metal matrix composites with light metals such as Al, Mg, and Ti as matrices and carbon and SiC as reinforcements are also playing an important role in transport and other industries. In contrast to the above two classes of composites, which are used mostly for their high specific strength, ceramic matrix composites mostly find their applications

for ultrahigh-temperature applications. In the recent past, nanocomposites, in which either the reinforcement or both the matrix and reinforcement are in the nanoscale, have found various structural and functional applications.

1.4 The coming of multicomponent HEAs

From the above description of conventional and special alloys, historically over five millennia, the alloy design, alloy production, and alloy selection were all based on one principal-element or one-compound concept. This alloy concept has generated numerous practical alloys contributing to civilization and daily life. But it still limits the degree of freedom in the composition of the alloy and thus restricts the development of special microstructures, properties, and applications. Consequently, materials science and engineering of alloys is not fully explored since those alloys outside this conventional scheme have not been included.

1.4.1 *Karl Franz Achard*

It should be mentioned that in the late eighteenth century, a German scientist and also metallurgist Franz Karl Achard had studied the multicomponent equimass alloys with five to seven elements (Smith, 1963). He could be most probably the first one to study multiprincipal-element alloys with five to seven elements. In many ways, he is the predecessor for the researches of Jien-Wei Yeh on HEAs. More than two centuries separate them. In 1788, Achard published a little-known French book “Recherches sur les Propriétés des Alliages Métallique,” the first compilation of data on alloy systems in Berlin. He disclosed the results of a laborious and comprehensive program on over 900 alloy compositions of 11 metals, including iron, copper, tin, lead, zinc, bismuth, antimony, arsenic, silver, cobalt, and platinum. Because of high cost, he studied fewer compositions with silver, cobalt, and platinum. For other elements, he made representative alloys of every possible combination of components up to seven components. Besides many binary, ternary, and quaternary alloys, he made quinary, sexinary, and septenary alloys only in equal proportions in weight. All the alloys were in the as-cast condition, and on these, he carried out tests for density; hardness; strength; impact resistance; ductility; the resistance to abrasion; the degree to which the alloy could be polished; and finally the results of exposing a polished surface to dry air, moist air, moist air with HCl acid fumes, and moist hydrogen sulfide. In this book, he pointed out that the properties of alloys are quite different from those of the pure metals and are unpredictable. Only experiment can instruct us. This book is mainly a report without any discussion. All the experimental results were given in tabular form. Although this book was written in French insisted upon by Frederick the Great, unfortunately, it was virtually ignored by metallurgists everywhere. This rare work was brought to light only in 1963 by Professor Cyril Stanley Smith (Smith, 1963).

Toward the end of the 20th century, two entirely independent investigations by Brian Cantor in the United Kingdom and Jien-Wei Yeh in Taiwan made a disruptive break with the classical tradition of alloying. A brand new alloy concept “HEAs” has

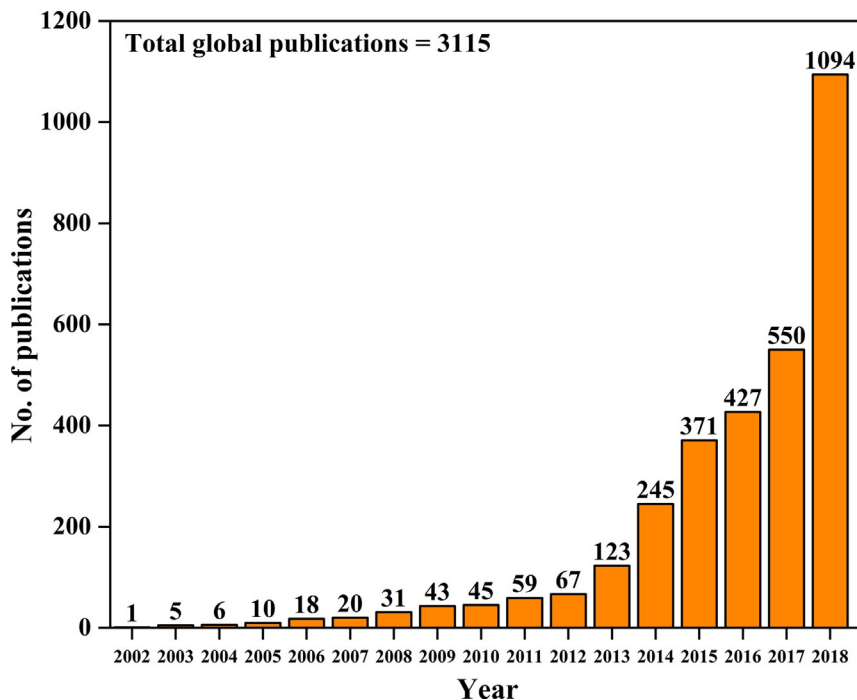


Fig. 1.4 Year-wise publications in the area of HEAs.

been proposed and explored and has led to a flurry of excitement. Fig. 1.4 gives the number of year-wise journal publications in the area of HEAs. The figure shows extraordinary growth in the past decade. The keywords used are HEAs and equiatomic multimetallic alloys. A number of reviews/overviews have been published in this area, which can be viewed at <https://mme.iitm.ac.in/hea/html/global/reviews.html>, the most comprehensive of these being one by [Miracle and Senkov \(2017\)](#). An edited volume in this field with the title “High-Entropy Alloys: Fundamentals and Applications” has been brought out by [Gao et al. \(2016a\)](#) through Springer. A number of conferences have HEAs as one of the important sessions. Yeh has initiated a biennial international workshop series, International Conference on High-Entropy Materials (ICHEM), in 2016, which was held in Taiwan. The second in the series has recently been held in December 2018 in Korea. Researchers in India are very active in this field with the pioneering work of B.S. Murty, who initiated a biennial workshop series, International Workshop on High-Entropy Materials (IWHEM), which were held so far in 2015 (Chennai) and 2017 (Hyderabad). A website reflecting the research activities on HEAs, particularly from India, is being maintained by the group of B.S. Murty (<https://mme.iitm.ac.in/hea/>), which is updated monthly. A list of all the publications in this field can be obtained at this site.

1.4.2 Brian Cantor

The first work on exploring this brave new world was done in 1981 by Cantor with his student Alain Vincent. They made several equiatomic alloys mixing many different components in equal proportions. In particular, the world record multicomponent alloy consisting of 20 different components each at 5% is held by this study. It was noticed that only one alloy with a composition of $\text{Fe}_{20}\text{Cr}_{20}\text{Ni}_{20}\text{Mn}_{20}\text{Co}_{20}$ forms a single face-centered cubic (FCC) structure; Vincent was an undergraduate project student, and the work was only written at that time in his thesis at Sussex University.

After this initial experiment, there was a hiatus. Similar studies on a wider range of alloys were repeated with another undergraduate project student, Peter Knight, at Oxford in 1998. He achieved some similar results and some new ones and published his results in a thesis at Oxford. Finally, Isaac Chang repeated the work again in about 2000 at Oxford and finally published the results in the open literature by presenting at the Rapidly Quenched Metals conference in Bangalore in 2002, which was then published in the journal *Materials Science and Engineering A* in July 2004 (Cantor et al., 2004). In this paper entitled “Microstructural development in equiatomic multicomponent alloys,” several important conclusions were drawn. A five component $\text{Fe}_{20}\text{Cr}_{20}\text{Mn}_{20}\text{Ni}_{20}\text{Co}_{20}$ alloy, on melt spinning, forms a single FCC solid solution, which solidifies dendritically. Based on this composition, a wide range of six to nine component alloys by adding other elements such as Cu, Ti, Nb, V, W, Mo, Ta, and Ge exhibit the same majority FCC primary dendritic phase, which can dissolve substantial amounts of other transition metals such as Nb, Ti, and V. More electronegative elements such as Cu and Ge are less stable in the FCC dendrites and are rejected into the interdendritic regions. Besides, alloy containing 20 components, that is, 5 at.% each of Mn, Cr, Fe, Co, Ni, Cu, Ag, W, Mo, Nb, Al, Cd, Sn, Pb, Bi, Zn, Ge, Si, Sb, and Mg, and another alloy consisted of 16 elements, that is, 6.25 at.% each of Mn, Cr, Fe, Co, Ni, Cu, Ag, W, Mo, Nb, Al, Cd, Sn, Pb, Zn, and Mg, are multiphase, crystalline, and brittle both in as-cast condition and after melt spinning. Surprisingly, however, the alloys consisted predominantly of a single FCC primary phase, containing many elements but particularly rich in transition metals, notably Cr, Mn, Fe, Co, and Ni. Finally, the total number of phases is always well below the maximum equilibrium number allowed by the Gibbs phase rule and even further below the maximum number allowed under nonequilibrium solidification conditions.

It is also important to point out that Cantor came up with another novel idea of equiatomic substitution later, in the early 2000s (Kim et al., 2003a), as a method of exploring metallic glass. These compositions are also in this vast uncharted region of material space.

1.4.3 Jien-Wei Yeh

J. W. Yeh independently explored the multicomponent alloy world since 1995 (Yeh et al., 2004b; Hsu et al., 2004). Based on his own concept that high mixing entropy factor would play an important effect in reducing the number of phases in such high-order alloys and render valuable properties, he supervised a master student

K.H. Huang in 1996 to start the research and see the possibility of success in the fabrication and analysis of HEAs. Around 40 equiatomic alloys with five to nine components were prepared by arc melting. Investigations were made on microstructure, hardness, and corrosion resistance in as-cast state and fully annealed state. The alloy design is mainly based on commonly used elements. From those data of around 40 compositions, 20 alloys based on Ti, V, Cr, Fe, Co, Ni, Cu, Mo, Zr, Pd, and Al, with or without 3 at.% B addition, were selected as experimental alloys in the MS thesis of Huang in 1996 (Huang and Yeh, 1996, published as MS thesis of National Tsing Hua University, Taiwan).

Based on this study, typical dendritic structure was seen in the as-cast structure. All alloys have high hardness level in the range from 590 to 890HV depending on the composition and fabrication conditions: as-cast or fully annealed. Full annealing treatment in general retained similar hardness level of as-cast state. Higher number of elements increased the hardness, but nine-element alloys more or less displayed a small decrease in hardness. Small addition of B has led to some increase in hardness.

In the discussion on these trends, high hardening due to large lattice distortion and stronger bonding was proposed. All these alloys in general displayed very good corrosion resistance assessed by the weight loss after immersion in four acidic solutions of HCl, H₂SO₄, HNO₃, and HF, each in 0.01 and 1 M, for 24 h. The addition of passive elements and the benefit of low free energy due to high entropy were thought to contribute to corrosion resistance. This study thus led to valuable suggestions about high-entropy effect, lattice distortion effect, and slow diffusion effect. After this study, two more studies were made before 2000 on different aspects of HEA and were submitted as theses (Lai et al., 1998; Hsu et al., 2000, all published as MS theses of National Tsing Hua University, Taiwan). During 2001–2003, nine different studies were conducted by Yeh's group: five studies on HEA bulk alloy concerning with deformation behavior, wear behavior, and annealing behavior; two studies on HEA thin films deposited by magnetron sputtering; and two on HEA thermal spray coatings (Huang et al., 2001; Chen et al., 2002; Tung et al., 2002; Chen and Lin, 2003; Huang and Yeh, 2003; Hsu et al., 2003; Lin et al., 2003, Tsai et al., 2003a; Tsai et al., 2003b, all published as MS theses of National Tsing Hua University, Taiwan). Until 2017, Yeh has supervised 98 MS theses and 12 PhD theses in this exciting area of HEAs. Besides the supervision by Yeh, a portion of some of these theses on HEAs and related materials were also supervised by his colleagues and collaborators, namely, S.K. Chen, S.J. Lin, T.S. Chin, J.Y. Gan, and T.T. Shun.

Yeh had submitted the "HEA concept" paper to *Science* on January 2003 but was not accepted by *Science*. After this, he submitted the same paper to *Advanced Materials* and then agreed the transfer to the sister journal, *Advanced Engineering Materials*, for publication. In May 2004, this paper entitled with "Nanostructured high-entropy alloys with multiprincipal elements—novel alloy design concepts and outcomes" was published. It becomes the first one to elucidate the concept of HEAs by providing experimental results and related theory (Yeh et al., 2004b). Besides this, another paper entitled "Multiprincipal-element alloys with improved oxidation and wear resistance for thermal spray coating" was published in *Advanced Engineering Materials* in February 2004 (Huang et al., 2004). But the term of HEA was not used

in this paper. Two papers entitled “Wear resistance and high-temperature compression strength of FCC CuCoNiCrAl_{0.5}Fe alloy with boron addition” and “Formation of simple crystal structures in solid-solution alloys with multiprincipal metallic elements” were published in *Metallurgical and Materials Transactions A* later in the same year (Hsu et al., 2004; Yeh et al., 2004a). Before the submission of the first of the above paper, Yeh had applied for HEA patents in Taiwan (10 December 1998), Japan, the United States, and mainland China.

1.4.4 Srinivasa Ranganathan

It should be mentioned that S. Ranganathan has also spent long time to think and look into such multicomponent alloys unexplored by people. Through the communications and discussions on this unknown field with J.W. Yeh, he published a paper entitled “Alloyed pleasures—multimetallic cocktails” to introduce three new alloy areas: bulk metallic glasses by A. Inoue, superelastic and superplastic alloys (or gum metals) by T. Saito, and HEAs by J.W. Yeh in *Current Science* in November 2003 (Ranganathan, 2003). This becomes the first open publication in journals on HEAs, which led to the activation of this new field.

In this article, he said that the multicomponent alloys represent a new frontier in metallurgy. They require hyperdimensions to visualize. If we use a coarse mesh of 10 at.% for mapping a binary system, the effort involved in experimental determination of phase diagrams rises steeply. Thus, the effort of experimental determination of

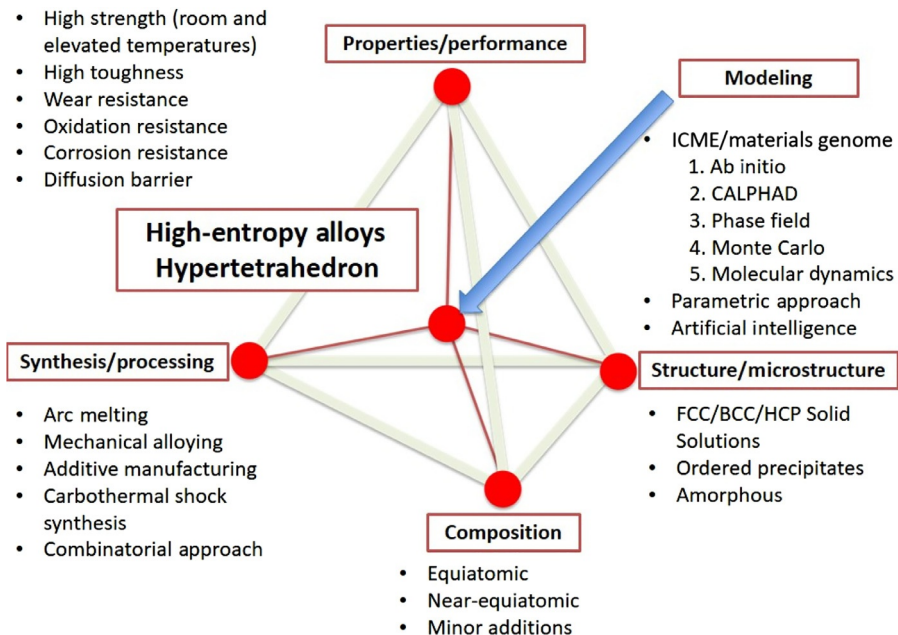


Fig. 1.5 The material hypertetrahedron for HEAs.



Fig. 1.6 The cover of 30 March 2018 issue of the journal *Science*, showing a multicomponent alloy prepared by carbothermal shock synthesis.

a seven-component system will be 10^5 times that of a binary diagram and will alone need as much effort as has been spent over the last 100 years in establishing ~ 4000 binary and ~ 8000 ternary diagrams. While the computation of phase diagrams from first principles has made impressive progress in the last decade, the calculation of higher order systems is a daunting task. In this scenario, we have explorers like A. Inoue, T. Saito, and J.W. Yeh pointing to exciting new alloys with applications.

1.5 The scope of this book

From the open publications by the three initiators mentioned above, HEAs have become an emerging field with many more researcher's efforts and contributions. In a broad view, many aspects have been explored and researched. Fig. 1.5 shows the material hypertetrahedron for the HEAs, which shows in a nutshell the broad spectrum of research and development that is taking place in this field. Based on this, the content of this book has been designed to cover this broad spectrum. Chapter 2 gives the basic definition of HEA and the compositional notations. Chapter 3 describes the key aspects of physical metallurgy of HEAs, namely, diffusion, phase transformations, and fundamental mechanisms of deformation. Chapter 4 describes the factors affecting the phase selections and gives the parametric approaches to design alloy compositions. Chapter 5 describes the different simulation and modeling methods involved in integrated computational materials engineering (ICME) and material genome initiative (MGI). Artificial intelligence has brought about a paradigm change where the discovery, development, and design of alloys can make progress without human intervention also. Chapter 6 describes the different synthesis methods used for HEAs. Chapter 7 describes the formation of solid solutions and their microstructure in different HEA compositions. Chapter 8 describes the special subgroups found in HEAs including intermetallics, interstitial compounds, metallic glasses, and eutectic and refractory HEAs. Chapter 9 describes the HEA-related materials such as HE oxides, HE carbides, HE nitrides, HE diborides, and composites. Chapter 10 describes the HEA coatings in thin and thick films. Chapters 11 and 12 describe the structural and functional properties, respectively. Finally, Chapter 13 describes property goal pursued, potential advanced applications, and future trends. As for the interconnections in the HEA hypertetrahedron, all chapters also emphasize them with an aim to give comprehensive understanding on HEAs.

The explosion in the number of publications, special issues, and conferences testify to the vigorous growth in the field. The cover of the journal *Science* captures the current position. Fig. 1.6 shows a multicomponent alloy prepared by shock synthesis taking us back to the technique employed by Pol Duwez in 1959. Powerful characterization techniques allow us to see each individual atom. This is not only a scientific tour de force but also a significant attachment as the particles show catalytic properties. The different colors show different elements on the surface of the particle.