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Growing designability in structural materials

Structural materials are critical components for our daily lives and industries. This Comment highlights the emerging concepts in structural materials over the past two decades, particularly the multi-principal element alloys, heterostructured materials and additive manufacturing that enables the fabrication of complex architectures.

Robert O. Ritchie and Xiaoyu Rayne Zheng

Although never as 'glamorous' in the world of materials science as quantum and electronic materials, perovskites or graphene, in many respects structural materials provide the framework for our civilization. The integrity of structural materials ensures the safety of our infrastructure (from buildings to bridges), the basis of our transportation (from automobiles and ships to aerospace), and the critical components for energy and power generation (from pipelines and nuclear pressure vessels to high-temperature power turbines). Over the past two decades there have been many advances in structural materials to enable safer planes, lighter cars, improved infrastructures, more efficient power supplies and the like. However, as many potential applications — such as aerospace, nuclear and hypersonics — call for materials to withstand more extreme environments, there remains the omnipresent quest to develop superior structural materials for the future that can perform at a lighter weight, under higher stresses and in such extreme conditions, including corrosive environments, intense impact loading and at very high or very low temperatures, to support advances in these strategic fields. Implicit in this quest are cost, environmental and sustainability concerns, and strategic issues.

In this Comment, we briefly describe some of the relatively new concepts in structural materials that have emerged over the past two decades and have largely expanded the design space in the field. In many cases, these materials have yet to be 'used in earnest', and some are still clearly in the realm of academic research, but they do represent exciting directions with the potential of developing materials with unprecedented mechanical performance.

In the past two decades, many structural metallic alloys commonly used in practice have seen notable progress, for instance, the corrosion-resistant high-performance aluminium alloys, the improvement in mechanical properties for various titanium alloys and steels that make use of transformation- and/or twinning-induced plasticity (TRIP and TWIP, respectively) effects[1], ductile and biodegradable magnesium alloys, development of bulk metallic glasses, and much more. Such progress has been accompanied by markedly better understanding of the interplay between the properties and microstructures of both crystalline and amorphous metals.

With respect to non-metallic materials, composites have truly 'come of age' in the engineering landscape. Carbon-fibre-reinforced plastics[2], developed some half a century ago, were first used for the fuselage of a commercial passenger aircraft in 2009, the Boeing 787 Dreamliner, representing a lighter-weight alternative to aluminium alloys. Shortly afterwards, ceramic-matrix composites began to appear in commercial gas-turbine engines, for example, in the GE/Safran's LEAP turbofan used to power the Airbus A320. Specifically, silicon carbide continuously reinforced with SiC fibres (SiC/SiC) are now being used for non-rotating parts such as vanes and seals, as they have one-third of the density of Ni-base superalloys and can operate at much higher temperatures[3]. Once thought to be hopelessly brittle for such applications, these ceramics have a weak fibre/matrix interface that allows the fibres to hold the material together once the matrix has fractured, giving rise to a form of 'ductility' between the proportionality limit (the 'effective yield stress' at matrix failure) and the maximum load at failure (when the fibres break). This is achieved using boron-nitride-fibre coatings, although the nuclear industry is developing similar SiC/SiC composites with pyrolytic-carbon-fibre coatings as a cladding material for nuclear fuel containment to replace zirconium alloys, and in the longer term for future nuclear fusion applications[4].

Beyond the structural materials that have been pursued for many decades and even centuries, the exciting topics on the science-based discovery of new materials in the past 20 years have come in the development of multiple-principal-element or high-entropy alloys (HEAs), bioinspired and more generally heterostructured materials, additive manufactured alloys, and lattice/metamaterials (Fig. 1). With exceptions, they have few current applications, in part due to the long lead time from lab discovery to industrial use; unlike electronic materials, this can often be measured in decades for new structural materials. Nevertheless, all these new classes of materials have excellent potential, especially as their future development may well be accelerated by substantial advancements in processing, such as the use of additive manufacturing methodologies.

The concept of HEAs began in 2004 with the search for metallic alloys at the centre of phase diagrams rather than at the edges[5], and by attempting to avoid the presence of undesirable compounds by promoting configurational entropy (with approximately five principal elements) relative to the enthalpy of phase formation[6]. The field today, however, has developed into a far larger mission for the discovery of new compositionally complex materials with improved properties[7]. The emphasis is still principally with mechanical properties but with increasing interest in other material classes — glasses and ceramics — and in functional materials for batteries and catalysis[8]. However, despite significant recent advances with the properties of these alloys, as described below, cost is likely to always represent some degree of impediment to their application because of their multiple-principal-element compositions.

With the almost exponential growth of publications on HEAs — some 15,000 largely over the past decade — two main classes of metallic alloy have emerged. The first of these is the face-centred cubic HEAs based on the original single-phase equiatomic CrMnFeCoNi (Cantor) alloy. These alloys display exceptional damage tolerance, with strengths of ~1 GPa, tensile ductilities >60% and fracture toughnesses >200 MPa $m^{0.5}$, which are further enhanced at cryogenic temperatures[9]. This results from a progressive sequence of synergetic deformation mechanisms — dislocation glide, stacking-fault formation, nanotwinning and in situ phase transformation — that induces prolonged,

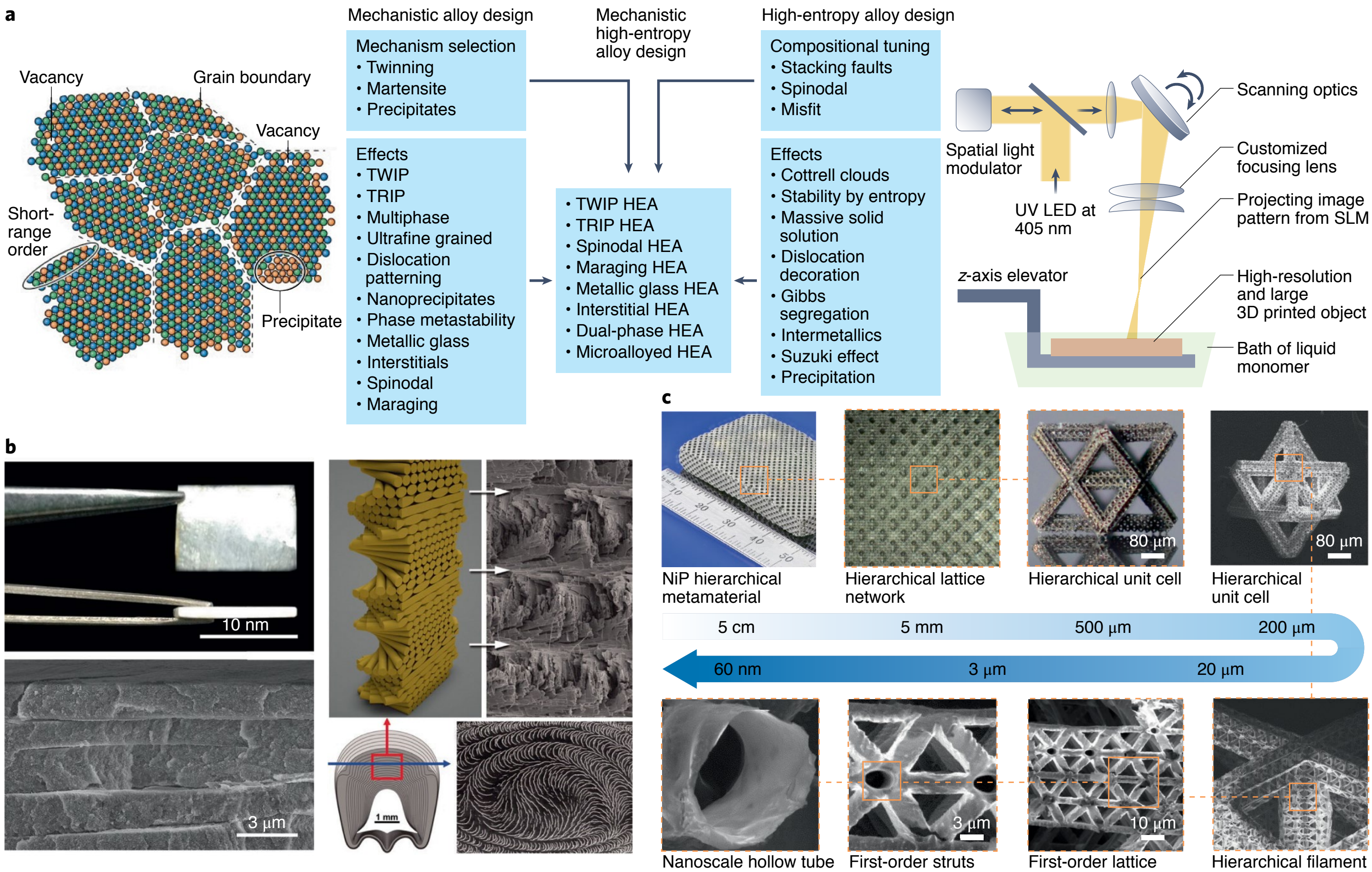

Fig. 1 | Expanding designability of structural materials in the past two decades. a, Multiple-principal-element alloys[7]. Left panel: a schematic of HEA with some typical defects[7]. Spheres with different colours represent different elements. Right panel: HEA design combined with established effects from conventional alloys. **b**, Examples of bio and bio-inspired hierarchical structures. Left panel: brick-and-mortar nacre-inspired structure[13]. Right panel: chitin fibril helicoidal structural motif within the periodic region (with periodicity ~75 μm) in the stomatopod dactyl club[15]. **c**, A lightweight, super-elastic multiscale metallic (nickel alloy) metamaterial with feature sizes across seven orders of magnitude, which is printed by a large-area projection micro-stereolithography technique as shown in the schematic in the top right[24]. UV, ultraviolet; LED, light-emitting diode; SLM, spatial light modulator. Figure adapted with permission from: **a**, ref. [7], Springer Nature Ltd; **b**, left panel, ref. [13], AAAS; **b**, right panel, ref. [15], AAAS; **c**, ref. [24], Springer Nature Ltd.

continuous strain hardening to promote strength yet, at the same time, to delay necking instabilities to increase ductility[8]. Indeed, at 20 K, the single-phase equiatomic CrCoNi alloy appears to exhibit the highest fracture toughness on record.

The second class is the body-centred cubic alloys, which can comprise refractory elements and, as such, are noted for their high strength at elevated temperatures (often exceeding that of Ni-base superalloys). Indeed, these refractory high-entropy alloys (RHEAs) have provided a potential new paradigm for high-temperature materials, in the form of a largely unexplored, compositional space for discovery[10]. Many alloy compositions have already been shown to display ultrahigh strengths; some, such as NbTaHfZr, exceed 2.5 GPa at ambient temperatures, but others, such as MoNbTaVW, retain high strengths of ~800 MPa at temperatures as high as 1,500 °C. However, these RHEAs often have poor oxidation resistance with minimal tensile ductility due to their high ductile–brittle transition temperatures and often embrittled grain boundaries. The future challenge here is to find combinations of elements and appropriate microstructures that can retain high-temperature strength without comprising tensile ductility, as many of the current RHEAs exhibit grossly inadequate fracture toughness.

Whereas functional materials based on nature have been developed, such as adhesives based on DOPA (3,4-dihydroxyphenylalanine) from mussels[11], the application of bioinspired structural materials is rare. Nevertheless, in the realm of scientific discovery, this topic has become intensely active over the past two decades with advances such as tough ceramics and composites mimicked on the brick-and-mortar nacre structure in mollusc shells[12,13], concepts of lightweight armour based on fish scales[14], and super-hard structures based on the appendage of the mantis shrimp[15], to name but a few (Fig. 1b). Nature generally designs its structural materials as composites of hard and soft phases, but with highly complex hierarchical architectures spanning multiple length scales[12]. Natural materials often display rare combinations of properties that are generated at different length scales from the ingenious use of gradients — in composition, in microstructural arrangement, orientation and distribution, and through graded interfaces[16]. Mimicking such complexity in bioinspired synthetic materials is a major challenge, at least with traditional 'top-down' processing, but with the rapid development of additive techniques, such as three-dimensional printing, it is becoming possible to build such materials 'bottom-up' to realistically generate nano- and microscale structures into macroscale materials[12]. Nowhere is this more evident than in the rapid development of architected, cellular and lattice materials, which come under the general heading of metamaterials.

The need to increase energy and fuel efficiency in aerospace and automotive vehicles has driven the development of such low-density structural materials. Whereas solid materials are significantly heavier than water, materials that contain networks of cellular topology could offer significant energy absorption and resilience at a fraction of the weight compared with their solid counterparts. For more than half a century, honeycombs have been used almost exclusively for these purposes because they can be readily manufactured by expansion, corrugation and cutting processes. Compared with natural cellular architectures with intricately shaped hollow cells, gradients and structural hierarchies, man-made cellular architectures are much less sophisticated.

With significant advances in additive manufacturing technologies over the past decade, many lightweight structural materials with more complex architectures, structural hierarchies and material choices have emerged and been created. These lightweight materials are designed and optimized to have superior and tailored properties compared with honeycombs.

The first concepts began in the early 2010s with reports of structural metamaterials reaching the property white space, that is, a property combination that no existing materials are available to occupy[17–19]. At low densities, additive manufactured structural metamaterials extend the property space of existing metals, polymers and ceramics to previously unachievable regions with densities lower than 10 kg cm^{-3} and approaching 1 kg cm^{-3}, while achieving high strength and stiffness, as well as high recoverability under large strains (>40%). Indeed, new developments in structural metamaterials keep pushing the envelope of extremal properties, including low-density materials that reach the Hashin–Shtrikman stiffness bounds with exotic mechanical behaviour, such as negative mechanical indexes (negative Poisson's ratios and negative compressibility).

Although early in their industrial adoptions, their continued expansions have been propelled by the following fronts. Additive manufacturable feedstock has expanded to high-strength structural materials that have been used in standard top-down manufacturing. Significant progress in printable structural materials has enabled the development of printable alloys, including steels, aluminium alloys, Ni-Cr-based superalloys, titanium alloys (largely Ti-6Al-4V) and carbon-fibre-reinforced composites[20,21]. This has enabled the development of complex parts that cannot be manufactured with conventional casting and moulding processes. The caveat is that the as-printed bulk materials do not necessarily result in parts that meet performance-driven criteria and behaviour consistency for certification for wider-scale adoption (particularly in demanding environments), before forming structural metamaterials due to microstructural defects from printing uncertainties. Most mitigation strategies rely on tailoring microstructure and reducing defects via additional in situ process control and monitoring during printing, combined with predictive physics-based models[22].

Advances in additive manufacturing tools for larger volume and higher-resolution parts enable the realization of sophisticated structural metamaterials that span multiple structural hierarchies and larger dimensions (Fig. 1c). Since 2016, structural metamaterials have been gaining significantly more functionalities in many domains, including high-temperature metamaterials, advanced alloys and multi-functionalities. As these materials are scaled up to larger dimensions, accessing their sensitivity to structural damage and defects is critical to their structural applications. The conventional mechanics for continuous materials and testing protocols might not be adequate or accurate enough to characterize the behaviour of metamaterials comprising a network of discrete structural elements, as opposed to a continuum[23].

Artificial intelligence and topology optimization methods push the discovery of new metamaterial designs and accelerate their design–manufacturing cycles for custom applications. These advances have begun to push for commercial goods manufacturing where tailorable shapes and custom mechanical behaviour (tailorable stiffness, energy absorption and toughness) are desired, including helmet, shoe midsole and vehicle components design, and antenna architectures. New advances in these fronts will also need to account for process uncertainty and structural defects, as well as microstructural imperfections in the base material. ❐

Robert O. Ritchie[1,2] ✉ and Xiaoyu Rayne Zheng[1,2] ✉

[1]*Department of Materials Science & Engineering, University of California, Berkeley, CA, USA.* [2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.*
✉*e-mail: roritchie@lbl.gov; rayne23@berkeley.edu*

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Competing interests

The authors declare no competing interests.