

## Review



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### Author for correspondence:

Robert O. Ritchie

e-mail: [roitchie@lbl.gov](mailto:roitchie@lbl.gov)

# Toughening materials: enhancing resistance to fracture

Robert O. Ritchie

Materials Sciences Division, Lawrence Berkeley National Laboratory, and Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA

ROR, 0000-0002-0501-6998

It has been said that 'God invented plasticity, but the Devil invented fracture!' Both mechanisms represent the two prime modes of structural failure, respectively, plastic collapse and the rupture/breaking of a component, but the concept of developing materials with enhanced resistance to fracture can be difficult. This is because fracture resistance invariably involves a compromise—between strength and ductility, between strength and toughness—fundamentally leading to a 'conflict' between nano-/micro-structural damage and the mechanisms of toughening. Here, we examine the two major classes of such toughening: (i) *intrinsic toughening*, which occurs ahead of a crack tip and is motivated by plasticity—this is the principal mode of fracture resistance in ductile materials, and (ii) *extrinsic toughening*, which occurs at, or in the wake of, a crack tip and is associated with crack-tip shielding—this is generally the sole mode of fracture resistance in brittle materials. We briefly examine how these distinct mechanistic processes have been used to toughen synthetic materials—intrinsically in gradient materials and in multiple principal-element metallic alloys with the example of metallic glasses and high-entropy alloys, and extrinsically in ceramics with the example of ceramic-matrix composites—in comparison to Nature which has been especially adept in creating biological/natural materials which are toughened by one or both mechanistic classes, despite often consisting of constituents with meagre mechanical properties. The success of Nature has been driven by its ability to cultivate the development of materials with multiple length-scale hierarchical structures that display ingenious gradients and structural adaptability, a philosophy which we need to

emulate and more importantly learn to synthesize to make structural materials of the future with unprecedented combinations of mechanical properties.

This article is part of a discussion meeting issue 'A cracking approach to inventing tough new materials: fracture stranger than friction'.

## 1. Introduction

An essential quality of the vast majority of structural materials is that they display resistance to fracture, which means they must have *toughness*. However, they also must be able to sustain loads without permanently deforming, which means ideally they must have *strength*. Despite both being vital requirements of structural materials, unfortunately in the common vernacular, these two terms are often taken to mean the same thing, whereas in reality, for many material systems the properties of strength and toughness are actually mutually exclusive (figure 1a) [5]. Consequently, the process of developing damage-tolerant materials with resistance to failure is invariably an exercise in compromise—conferring toughness without compromise in strength.

Strength (or hardness) is invariably measured as a stress representing a material's resistance to non-recoverable (e.g. plastic) deformation (at least in ductile materials), while toughness is measured as an energy, or in terms of a critical 'crack-driving force',<sup>1</sup> to cause fracture. With respect to these two properties, strong materials which can undergo *limited* deformation can provide a critical contribution to toughness without excessive softening, as this enables the local dissipation of high stresses which would otherwise cause the material to fracture; this is why hard materials tend to be brittle, whereas lower strength materials, which can deform more readily, tend to be tougher. Among the different classes of materials, these deformation mechanisms can be quite diverse; dislocation plasticity is the most prominent in crystalline solids, but inelastic deformation can also occur via such processes as *in situ* phase transformations in certain metals and ceramics [6], shear banding in metallic glasses [7], the sliding of collagen fibrils in biological materials like tooth dentin and bone [8], the frictional motion between mineral platelets in seashells [9] and by microcracking in bone and geological materials<sup>2</sup> [10].

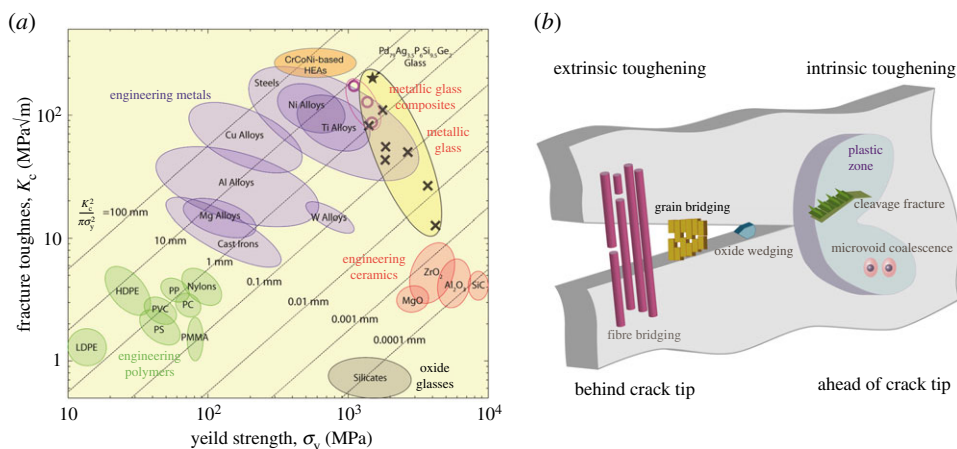
## 2. Intrinsic versus extrinsic toughening

We generally think of fracture as being either brittle or ductile. When a cracked body is subjected to a high stress, brittle fracture is idealized as the release of strain energy causing the severance of an atomic bond at the crack tip, whereas in ductile fracture the crack tip becomes blunted by such processes as dislocation emission from the tip. Whereas these events can be deemed as fundamental extremes of behaviour, it is often more useful to consider two major classes of toughening mechanisms in the presence of an incipient crack in real materials; I refer to these as *intrinsic* and *extrinsic* mechanisms (figure 1b) [5,11].

*Intrinsic toughening* pertains to developing resistance to micro-structural damage that is created ahead of the crack tip by such processes as the cleavage fracture of a grain, intergranular decohesion or the debonding of particles. The principal factor providing resistance here is plasticity (or more generally inelasticity), which has its origin mainly at the nanoscale, e.g. at the scale of a Burgers vector. Intrinsic toughening is an inherent property of a material; it acts to inhibit both crack initiation and growth, and is the prime mode of toughening in ductile materials.

<sup>1</sup>The 'crack-driving force' in fracture mechanics methodology is the governing parameter that characterizes the stress and displacement fields at a crack tip, e.g. the critical value of the linear-elastic stress intensity  $K$ , strain-energy release rate  $G$  or nonlinear-elastic  $J$ -integral, required to initiate and/or propagate a pre-existing crack.

<sup>2</sup>Distinct from dislocation plasticity, when materials deform inelastically by microcracking the stress-strain behaviour can be quite different in tension versus compression as cracks tend to close in compression. Moreover, whereas limited microcracking can be beneficial to toughness by inducing such inelasticity, excessive microcracking can be highly detrimental by resulting in macro-cracks and premature fracture.



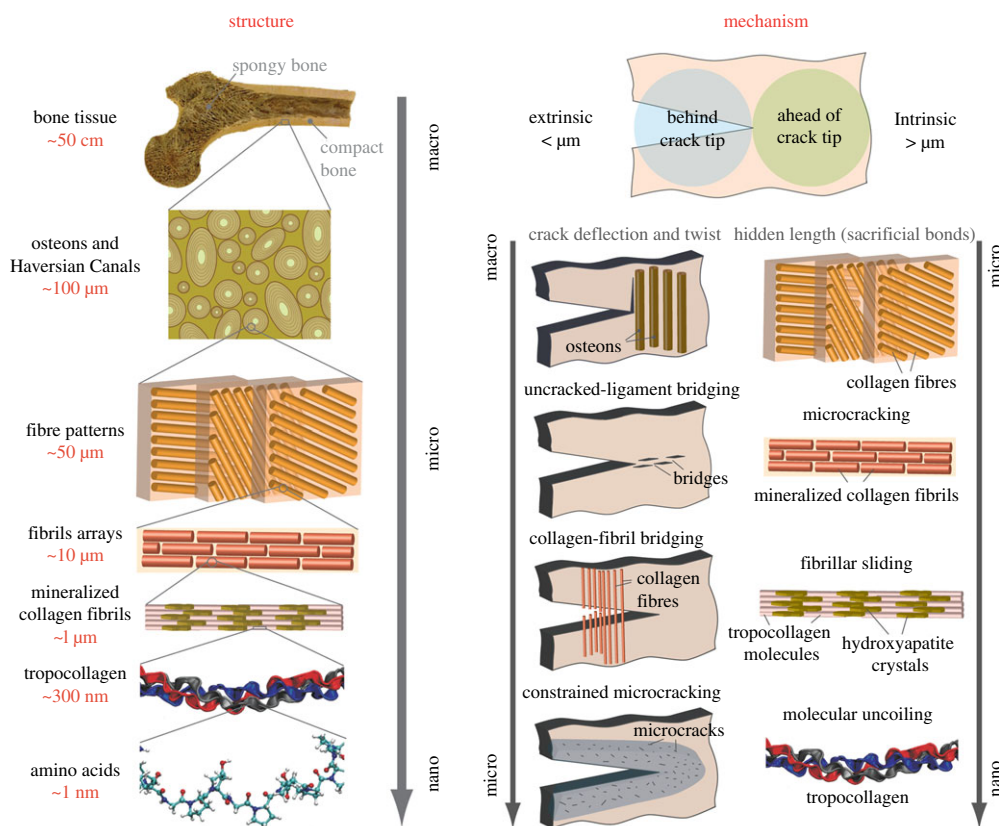
**Figure 1.** ‘Conflicts’ of strength versus toughness, showing (a) an Ashby plot of the strength–toughness relationships for engineering materials. Diagonal lines show the plastic-zone size,  $K_c^2/\pi\sigma_y^2$ , where  $K_c$  is the  $K_{I\text{-based}}$  fracture toughness and  $\sigma_y$  the yield strength. The black star and purple circles refer, respectively, to a Pd-based bulk-metallic glass [1] and glass-matrix composites [2], which are among the most damage-tolerant materials (in range of toughnesses in monolithic glasses is indicated by the black crosses). The toughest materials, however, are the CrCoNi-based high-entropy alloys (HEAs) [3,4]. (b) Schematic illustration showing how strength and fracture behaviour can be considered in terms of intrinsic (plasticity) versus extrinsic (shielding) toughening mechanisms associated with crack extension. Illustration shows mutual competition between intrinsic damage mechanisms, which act ahead of the crack tip to promote crack advance and extrinsic crack-tip shielding mechanisms, which act at, or primarily behind, the tip to impede crack advance. Intrinsic toughening results essentially from plasticity and enhances a material’s inherent damage resistance; as such it increases both the crack-initiation and crack-growth toughnesses. Extrinsic toughening acts to lower the local stress and strain fields at the crack tip; as it depends on the presence of a crack, it affects only the crack-growth toughness, specifically through the generation of a rising  $R$ -curve [5]. (Online version in colour.)

With rare exceptions, prototypical brittle materials such as ceramics cannot be toughened by promoting plasticity [12]. Here, even though the inherent fracture resistance can remain unchanged, *extrinsic toughening* mechanisms that act at, or principally behind, the crack tip can be effective in shielding the crack from the globally applied stresses/strains, thereby increasing the measured toughness. Extrinsic toughening results from such processes as crack deflection, transformation toughening or most commonly crack bridging, and thus can originate at multiple structural length-scales (often well into the micrometre range); it is a function of crack size (it, therefore, naturally leads to a crack-resistance or  $R$ -curve), and can only affect crack growth [5]. As noted above, this is generally the sole mode of toughening in brittle materials. Interestingly, due to the absence of plasticity, the strength of brittle materials is also governed by fracture<sup>3</sup>; accordingly, they can be toughened extrinsically without the need to induce ductility (as we generally understand it), and thus the ‘conflict’ between strength and toughness is not necessarily prevalent, as is apparent from the results for engineering ceramics in the Ashby plot in figure 1a.

### 3. Toughening in biological materials

Due to their hierarchical architectures spanning multiple structural dimensions, biological and natural materials often exhibit a combination of intrinsic and extrinsic toughening, as different mechanisms originate at different length-scales [13]. *Human bone* is an excellent example of this.

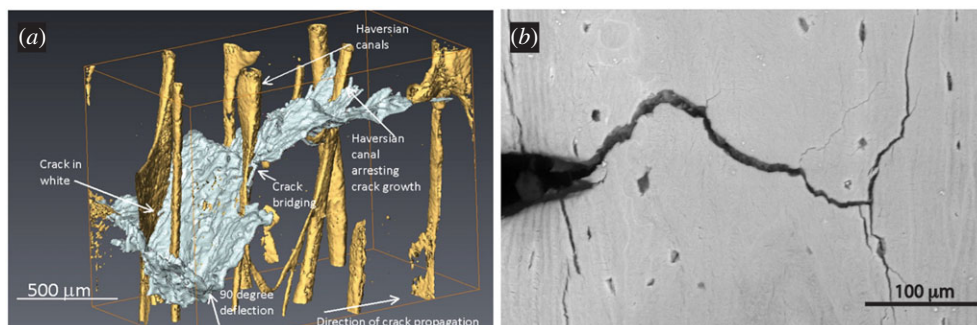
<sup>3</sup>Specifically, the strength of a brittle material is a function of its cohesive (atomic) bond strength, but its measured strength in any sample will also be governed by the distribution of existing flaws. For this reason, the tensile strength of ceramics is invariably lower in larger test specimens because there will be a higher statistical probability of sampling a larger defect. Indeed, Leonardo da Vinci discovered this in the fifteenth century while testing brittle wires when he found that long wires could carry less load than short ones with the same diameter.



**Figure 2.** The structure of bone showing (a) the seven levels of hierarchy [14] with (b) the prevailing toughening mechanisms [15]. At the smallest level, at the scale of the tropocollagen molecules and mineralized collagen fibrils, (intrinsic) toughening, i.e. plasticity, is achieved via the mechanisms of molecular uncoiling and intermolecular sliding of molecules. At coarser levels at the scale of the fibril arrays, microcracking and fibrillar sliding act as plasticity mechanisms and contribute to the intrinsic toughness. At micrometre dimensions, the breaking of sacrificial bonds at the interfaces of fibril arrays contributes to increased energy dissipation, together with crack bridging by collagen fibrils. At the largest length-scales in the range of 10 s to 100  $\mu\text{m}$ , the primary sources of toughening are extrinsic and result from extensive crack deflection and crack bridging by uncracked ligaments, both mechanisms that are motivated by the occurrence of microcracking. (Online version in colour.)

In figure 2, the so-called seven hierarchies of bone are schematically illustrated showing the nanoscale nature of the peptide chains which are twisted to form tropocollagen molecules, which in turn are twisted, with an added staggered array of hydroxyapatite crystals, to form mineralized collagen fibrils; these are further twisted together to create the collagen fibres at the micro-scale to form the lamellar structure of bone [14]. Within the cortical bone, at the scale of hundreds of micrometres, there are the osteonal structures (with Haversian canals at their centre), which provide the basis of the remodelling of bone, and at the macro-scale there is the bone itself with an outer shell of cortical bone and an inner network of trabecular bone.

Based on this multiple-scale architecture, intrinsic toughening, i.e. plasticity, derives mainly from a fibrillar sliding mechanism at the scale of tens to hundreds of nanometres, the length-scales associated with the mineralized collagen fibrils. With ageing, irradiation and certain diseases, however, the bone can embrittle due to increased cross-linking of the collagen [15], which inhibits this sliding mechanism; the intrinsic toughening then switches to higher length-scales and is accommodated by inelasticity associated with microcracking. However, a major source of toughness in bone is extrinsic and arises at much larger structural scales from crack bridging,



**Figure 3.** Crack deflection and twist promote extrinsic toughness. Another important extrinsic toughening mechanism in human cortical bone is crack deflection and twisting. When the growing crack is oriented nominally perpendicular to the osteons and Haversian canals in human cortical bone, crack deflection/bridging is particularly important. Here, the aligned interfaces within the osteon (i.e. the cement lines and lamellae) provide an interface where the crack often deflects as it extends. Crack deflection increases the toughness of bone because the local stress intensity at the crack tip requires a higher driving force for further crack extension. (a) 3D synchrotron computed micro-tomography of a fracture toughness sample after testing illustrates how a crack (blue) can grow from a notch in a wavy character with deflections and twists. (b) Crack deflections are also visible when using scanning electron microscopy (SEM) during crack extension. (In both images, the crack is advancing from left to right). (Online version in colour.)

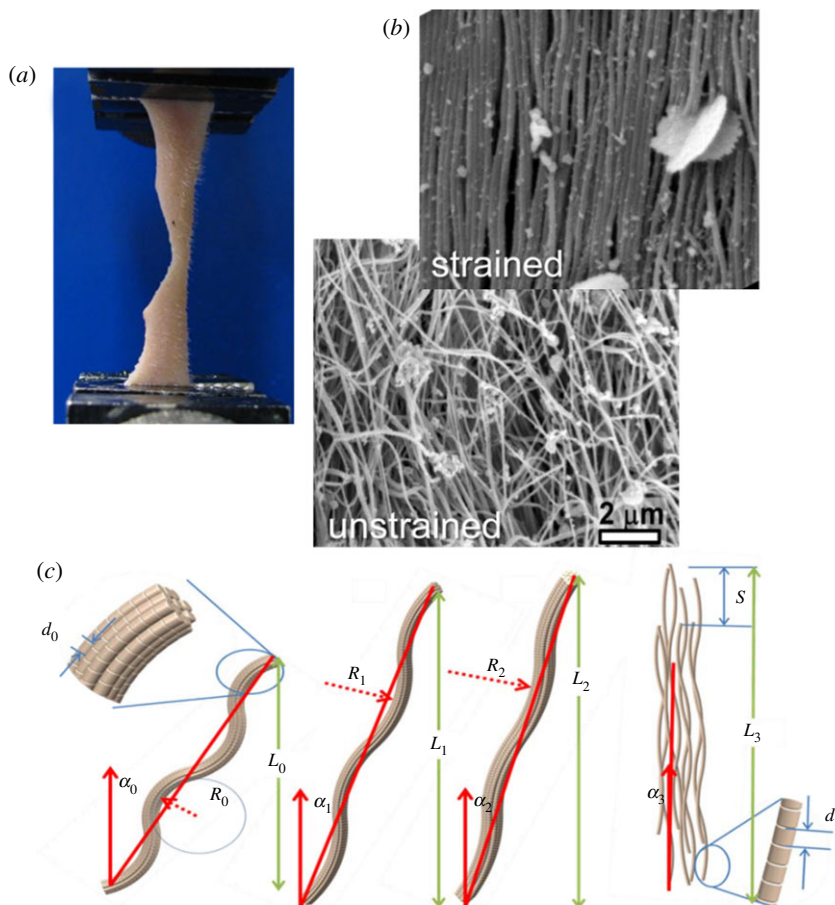
associated with uncracked regions between microcracks, and especially crack deflection as a growing crack encounters the more mineralized interfaces of the osteonal structures (figure 3) [16]; as the size and spacing of the osteons are in the range of tens to hundreds of micrometres, the characteristic length-scales for these deflection events can approach millimetre dimensions.

However, although the utilization of both intrinsic and extrinsic fracture resistance in Nature is omnipresent, e.g. in materials that comprise a hard and a soft phase, such as bone, tooth dentin, fish scales, etc. many natural materials rely solely on intrinsic toughening. Purely collagenous materials, such as skin, are a good example here. The *skin* consists of three layers—epidermis, dermis, endodermis—with mechanical properties dictated primarily by the dermis, the thickest layer. Its major constituents are Type-1 collagen and elastin: approximately 60% is collagen [17], which is primarily responsible for skin's mechanical properties; elastin accommodates the elastic deformation and is only relevant at low strains [18]. To fulfil its multifunctional role, skin must possess a tailored mechanical response to accommodate the body's flexibility and movement coupled with a sequence of damage minimization strategies to prevent tearing. Indeed, the tearing resistance of the skin is remarkable—it is essentially impervious to stress concentrations (figure 4a) which is associated with the morphology and behaviour of the collagen [19].

The collagen fibres in the dermis layer display a disordered, curvy morphology; they have a diameter of 5–10 μm and contain hundreds of approximately 50-nm diameter collagen fibrils (figure 4b). Skin's tear resistance can be directly attributed to the nano-/micro-scale behaviour of this collagen, specifically to the synergistic activation of several principal deformation mechanisms (figure 4c): the straightening of the individual collagen fibres within their initial disordered network, stretching of these fibres, their rotation towards the force application direction, their separation of the collagen fibres into fibrils and their stretching, sliding and eventual breakage in the tensile loading direction [19].

In fact, the role of collagen fibrils varies significantly in different biological materials. We have shown that in bone, stretching and sliding between collagen fibrils form the basis of plasticity (figure 2); in certain fish scales, the Bouligand-type structure, with collagen fibrils oriented in a twisted plywood formation, acts as a tough foundation to the highly mineralized surface to provide resistance to both penetration and fracture [20]. In both these cases, the collagen fibrils are mineralized and initially straight, whereas in the skin they are unmineralized, initially curvy





**Figure 4.** Skin displays remarkable tear resistance. (a) It is essentially insensitive to notches and stress concentrations. (b) The dermis layer consists of a disordered arrangement of curved collagen fibres (approx. 5–10 μm diameter), each of which is composed of hundreds of approximately 50 nm diameter collagen fibrils, which tend to align with straining. (c) Schematic of mechanisms of fibre and fibril deformation and failure under tension, showing the original configuration, the straightening and reorientation of the fibres, their separation into fibrils, and finally the stretching, sliding and eventually separation and breakage of the fibrils in the tensile loading direction [19]. (Online version in colour.)

and highly disordered, but their straightening, stretching, rotation and sliding serves to efficiently consume energy. The rotation mechanism is an example of adaptive structural reorientation which is often found in natural materials [21]; here it recruits collagen fibrils into alignment with the tension axis at which they are maximally strong to carry load or can accommodate shape change (e.g. blunting a tear); the straightening allows for strain uptake without much stress increase, stretching and sliding induces further energy dissipation during inelastic deformation. Such reorganization and sliding of the fibrils is responsible for stress redistribution (blunting) at the tips of tears and notches. It is the synergy of this sequence of mechanisms that confers the extraordinary resistance to tearing in skin [19], which in itself is a requisite for the survival of organisms.

## 4. Toughening in ceramic materials

As noted above, extrinsic toughening is the primary source, if not the only source, of toughening in brittle materials. In general, the intrinsic toughness of such materials is governed by the

strength of the covalent (or equivalent) atomic bonding at the crack tip, which in stress intensity terms is rarely much above  $1\text{--}3\text{ MPa}\sqrt{\text{m}}$ ; silicon with a  $K_{\text{IC}}$  fracture toughness value of approximately  $1\text{ MPa}\sqrt{\text{m}}$  is a good example. However, *monolithic ceramics*, such as zirconia, alumina, silicon carbide and silicon nitride, can be toughened extrinsically to  $K_{\text{IC}}$  toughnesses in the range of approximately  $8\text{--}15\text{ MPa}\sqrt{\text{m}}$  [12]. The tetragonal phase in partially stabilized zirconia can be induced to martensitically transform to a monoclinic phase in the high-stress region surrounding the crack tip; as this phase transformation involves a 4–6% dilation which is constrained by the surrounding untransformed material further away from the crack, the crack will extend into a region of compression within the transformation zone, leading to significant crack-tip shielding [22]. As such, the measured toughness of transformation-toughened zirconia can approach approximately  $15\text{ MPa}\sqrt{\text{m}}$ . Alumina, silicon carbide and silicon nitride can be similarly toughened by promoting crack deflection and in particular grain bridging. Intergranular fracture is an essential requirement here; the  $K_{\text{IC}}$  toughness of SiC is approximately  $2\text{--}3\text{ MPa}\sqrt{\text{m}}$  when it fractures transgranularly, whereas it can approach  $10\text{ MPa}\sqrt{\text{m}}$  for intergranular fracture [23], the key micro-structural feature being the presence of brittle nanoscale glassy films along the grain boundaries [24] which promotes boundary cracking, grain bridging and hence the higher toughness.

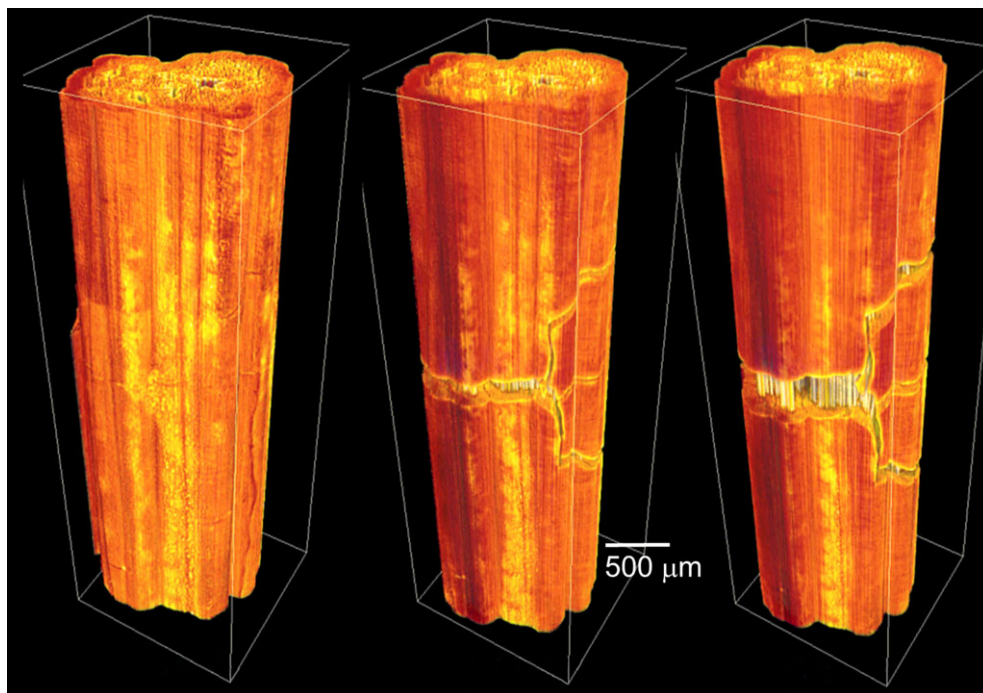
Despite these higher toughnesses, monolithic ceramics have rarely been considered for safety-critical applications, but *ceramic-matrix composites* have, most especially SiC–SiC composites for ultrahigh-temperature use. These materials, which comprise continuous SiC fibres within a SiC matrix, have found application as seals, vanes and combustion liners in new high-performance aircraft gas-turbine engines [25], where local temperatures can approach approximately  $1200^\circ\text{C}$ , and as potential coatings for nuclear fuel particles [26] in future Gen IV high-temperature reactors that will operate at approximately  $1000^\circ\text{C}$ . The key to their structural integrity is their extrinsic toughening from fibre bridging, as shown in the *in situ* computed micro-tomography scans of a  $1750^\circ\text{C}$  tension test on a silicon carbide containing a three-dimensional weave of SiC fibres in figure 5 [27]. The fibres are coated with boron nitride (pyrolytic carbon is used for the lower-temperature nuclear grade material) to provide a weak interface; this allows the fibres to deflect impinging cracks in the matrix and to pull-out yet remain intact after the matrix fractures. In this fashion, the material does not catastrophically break without warning, but rather is held together after the matrix fractures (at the proportional limit) by the intact fibres until they fail (at the ultimate tension strength); this effectively provides a form of ductility, which is invariably a requirement of structural materials for safety-critical applications.

## 5. Toughening in metallic materials

By contrast to ceramic materials, toughening in ductile materials, such as metals and alloys, is largely intrinsic, although crack deflection, if it occurs, can provide some extrinsic contribution to the fracture resistance. As examples of such intrinsic toughening, we examine here two relatively new classes of alloys based on the notion of multiple principal elements, namely bulk-metallic glasses (BMGs) and high-entropy alloys (HEAs), and also the concept of using gradient materials.

At first sight, BMGs would seem an unlikely candidate to overcome the problem of attaining strength with toughness. Admittedly, being amorphous, BMGs tend to be strong with strengths that can exceed approximately  $1\text{--}2\text{ GPa}$ , yet lacking dislocations, they deform by shear banding, which can lead to brittleness as a single shear band, formed in tension, can traverse a sample causing failure at vanishingly small strains. Ironically though, multiple shear-band formation provides the basis for plasticity in these glassy alloys, and hence offers a means to enhance their fracture toughness [1,2]. It is thus the key to making BMGs into structural materials, instead of merely ‘academic curiosities’. Indeed, with reference to the Ashby plot in figure 1*b*, certain BMGs and their composites represent some of the most damage-tolerant materials on record.

Atomistic origins for such multiple shear banding in BMGs have been suggested from molecular dynamics (MD) simulations (e.g. [28,29]). On the premise that the glassy state in BMGs is not purely amorphous but can contain local short- to medium-range order (SRO, MRO) in



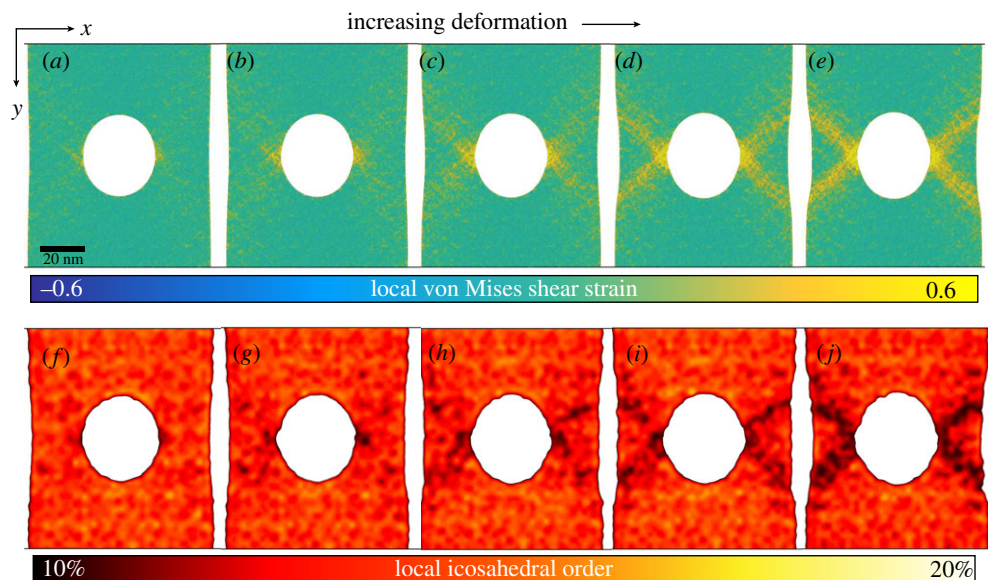
**Figure 5.** *In situ* three-dimensional computed micro-tomography images of a uniaxial tensile test of a three-dimensional woven continuous SiC fibre reinforced SiC-matrix composite under increasing tensile load at 1750°C, showing an example of extrinsic toughening by crack bridging. Tensile loading is applied longitudinally along the sample. A transverse crack in the matrix is first formed but the sample is held together by intact fibres which span the crack and carry load that would otherwise lead to catastrophic failure [27]. (Online version in colour.)

the form of motifs of atoms with local icosahedral symmetry, certain motifs with less dense packing and less five-fold symmetry, termed geometrically unstable motifs or GUMs, are thought to trigger the onset of shear banding due to their instability [28,29]. MD simulations show that clusters of GUMs can initiate shear localization in BMGs with the further propagation of the shear bands being accompanied by the breakdown of full icosahedral clusters as a structural signature.

Irrefutable experimental verification of this fascinating phenomenon has not, as yet, been realized but recent studies using a combination of *in situ* nanobeam electron diffraction in the transmission electron microscope with an ultrafast direct electron detector, coupled with the large-scale MD simulations, has been able to directly observe changes to the local short- to medium-range atomic ordering during the formation of a shear band at a notch in a  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  glass [30]. A spatially resolved reduction in local order prior to shear banding was detected due to increased strain, in agreement with the MD simulations where a similar reduction in local order could be related to the activation of a shear transformation zone (figure 6). These results thus provide some insight into how one could increase ductility in glassy materials by tailoring atomic order. They are also consistent with the somewhat paradoxical results that annealing can make BMGs more brittle, whereas quenching (which is known to induce GUMs) can make them more ductile, and that trace hydrogen additions, instead of causing embrittlement, can result in GUMs, thereby promoting both deformability and toughness (e.g. [31]).

By contrast, toughening in HEAs represents a somewhat more traditional means of intrinsic toughening in metallic materials. HEAs contain multiple principal elements but in nominally equal molar ratios [32,33], yet they can crystallize as a single phase, despite containing elements with different crystal structures. The original rationale for the thermodynamic stability of these materials was that the configurational entropy contribution to the total free energy in alloys



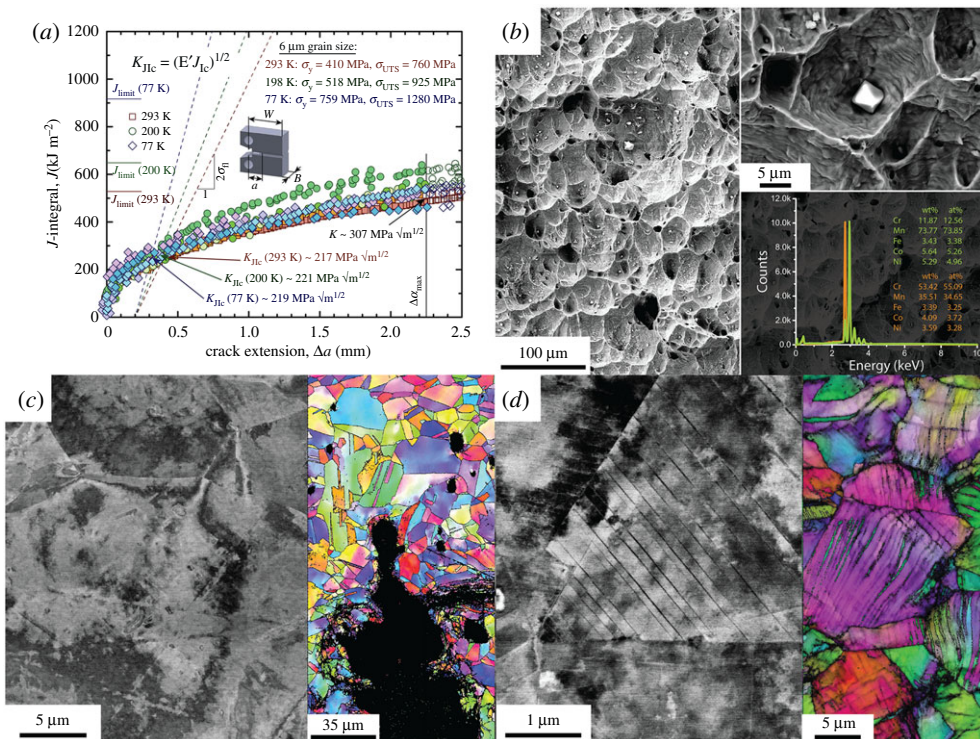


**Figure 6.** Theoretical simulations to discern the relationship between local icosahedral order and the occurrence of shear bands in BMGs. Five frames of MD-simulated  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  metallic glass at the strain of 4%, 5%, 6%, 7% and 8%, respectively, under uniaxial tensile deformation. (a–e) a colour map of local von Mises shear strain and (f–j) describe the spatial distribution of local icosahedral order in coarse-graining scale, for such five frames [30].

with five or more major elements would stabilize the solid-solution state relative to multi-phase microstructures [32], although the universal nature of the entropy argument for HEAs is now considered to be questionable [34,35]. However, in light of the seemingly infinite number of such alloys that remain unexplored, the field has not surprisingly taken the materials science discipline by storm, as shown by the plethora of publications which can be surveyed in several recent reviews [34–37].

Some of these alloys, in particular the face-centred cubic (*fcc*) CrCoNi-based alloys that are single phase, are especially notable for their mechanical behaviour in that they display truly exceptional, indeed remarkable, mechanical performance in the form of strength, ductility and toughness, properties that can be further enhanced at cryogenic temperatures [35]. The first of these alloys, the so-called Cantor CrMnFeCoNi alloy [33], was found to display a tensile strength that increases from 760 MPa to greater than 1.2 GPa, a tensile ductility increasing from 50% to 75%, with a  $K_{\text{JIC}}$  fracture toughness exceeding 200 MPa $\sqrt{\text{m}}$ , as temperatures were reduced from ambient to 77 K (figure 7) [3]. A three-component version of this alloy, CrCoNi, actually exhibited even better properties: at 77 K, this alloy had a tensile strength of 1.4 GPa, a tensile ductility of approximately 90%, a crack-initiation  $K_{\text{JIC}}$  fracture toughness exceeding 270 MPa $\sqrt{\text{m}}$  and a crack-growth toughness (after 2.2 mm of stable crack extension) of approximately 450 MPa $\sqrt{\text{m}}$  (figure 8) [4]. Comparing these values with that of the toughest titanium alloys where  $K_{\text{IC}} < 100$  MPa $\sqrt{\text{m}}$ , or silicon and graphene where  $K_{\text{IC}}$  is, respectively, approximately 1 and 4 MPa $\sqrt{\text{m}}$  [39], one can realize how tough these alloys actually are. Indeed, although they are not as strong as some of the metallic glasses, these HEAs are arguably the toughest materials on record (figure 1a), and ideally suited for low-temperature structural applications.

The immediate question is why are these *fcc* HEAs so damage-tolerant, particularly at cryogenic temperatures? Well, in addition to not suffering a ductile-to-brittle transition at low temperatures like body-centred cubic materials (these *fcc* HEAs fail by ductile microvoid coalescence at all temperatures down to 10 K (e.g. figure 7b)), the main reason is the creation of potent intrinsic toughening due to a steady, continuous source of strain hardening; this naturally

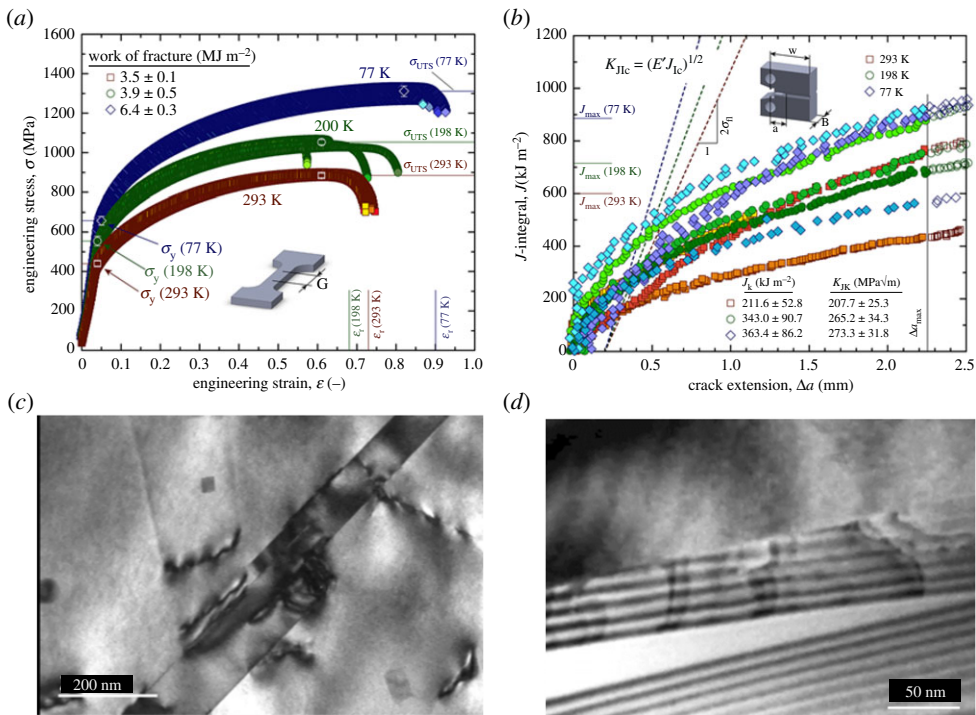


**Figure 7.** Fracture toughness, failure mechanism and deformation modes in the CrMnFeCoNi Cantor high-entropy alloy: (a)  $J$ -integral based crack-resistance curves show an increasing crack propagation resistance with crack extension, with  $K_{IIc}$ -based crack-initiation toughnesses for all tested temperatures (293 K, 198 K, 77 K) in excess of  $200 \text{ MPa}\sqrt{\text{m}}$  and crack-growth toughnesses above  $300 \text{ MPa}\sqrt{\text{m}}$ . (Note that  $J = K_I^2/E'$ , where  $K_I$  is the mode I stress intensity and  $E'$  is the plane-strain Young's modulus). (b) Failure is associated with 100% ductile fracture by microvoid formation from Cr- or Mn-rich particles and their coalescence. (c) Room temperature deformation involves dislocation activity evident from grain misorientations and cell structure formation. (d) At 77 K, deformation-induced nano-twinning occurs as an additional deformation mechanism, as seen in both back-scattered electron microscopy images and electron back-scattered diffraction maps [3]. (Online version in colour.)

increases the strength but it simultaneously delays the onset of the tensile necking instability, thereby extending the uniform elongation to 'defeat' the strength versus toughness conflict. The reason for this at the nano-/micro-scale is the existence of a duality of function in the form of a synergy of active deformation mechanisms that serve both to enhance strength and ductility.

Due to their multiple elements, these concentrated solid-solution alloys display high lattice friction but also very low stacking-fault energies, typically less than  $20 \text{ mJ m}^{-2}$ , both properties which we believe are affected by the existence of local chemical order [40–42]. This leads to a sequence of deformation mechanisms, in the CrMnFeCoNi alloy by the slow motion of undissociated  $1/2(110)$  dislocations along planar slip bands to promote strength and by the highly mobile activity, at somewhat higher strains, of Shockley partial  $1/6(110)$  dislocations to promote ductility [38,43]. Moreover, these mechanisms are augmented at lower temperatures by the onset of deformation nano-twinning (figure 7d), which further enhances the strain hardening to result in outstanding levels of fracture toughness [3].

Owing to its higher strength, the corresponding CrCoNi alloy can activate such nano-twinning (which is stress-controlled) even at ambient temperatures. This alloy develops a three-dimensional hierarchical twin network, which again serves a dual function: the twin (and grain) boundaries provide conventional boundary strengthening by arresting dislocations that impinge on them (figure 8c), yet for ductility, the twin boundaries themselves can act as 'highways' for



**Figure 8.** Strength, ductility and fracture toughness, and deformation modes in the CrCoNi alloy [4]: (a) uniaxial tensile stress/strain curves showing increasing strength and ductility with decreasing temperature from 293 to 77 K. (b)  $J$ -based crack-resistance curves show an increasing crack propagation resistance with crack extension,  $K_{Ic}$ -based crack-initiation toughnesses increasing from 208  $\text{MPa}\sqrt{\text{m}}$  at 293 K to 273  $\text{MPa}\sqrt{\text{m}}$  at 77 K, and crack-growth toughnesses above 450  $\text{MPa}\sqrt{\text{m}}$  at 77 K [4]. (c) Conventional boundary strengthening by the arrest of dislocation pile-ups that impinge on twin boundaries. (d) Movement of leading and trailing pairs of partial dislocations on the coherent twin-boundary plane; above approximately 8% global strain, partial dislocation pairs glide on the twin boundaries, which served as channels for dislocation movement [38]. (Stacking faults between leading and trailing partials are not visible). (Online version in colour.)

the glide of partial dislocations along, and cross-slip between, intersecting twin-boundary / matrix interfaces (figure 8d) [38]. As the stable twin architecture is not disrupted by interfacial dislocation glide, it can provide a continuous source of strength, ductility and toughness.

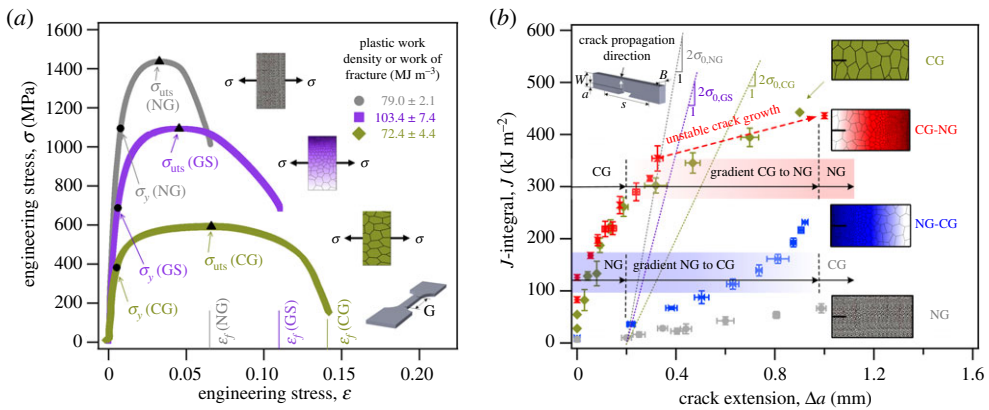
These potent sources of intrinsic toughening are also found in materials as old as Hadfield's Mn steel and as new as TRIP (transformation-induced plasticity) and TWIP (twinning-induced plasticity) steels [35]; indeed, all these structural materials share some commonality in their sequence of deformation mechanisms, but their effect appears to be magnified, for reasons not totally clear, in these multiple principal-element alloys.

## 6. Gradient materials

One potential problem with multiple principal-element metallic alloys, however, is their cost; although they generally can be thermo-mechanically processed by conventional techniques, they regularly contain expensive elements. In light of this, a second, largely bioinspired, approach to developing new damage-tolerant structural materials has been to use simpler materials [44] and to take 'a leaf from Nature's playbook' by inducing desired mechanical properties through the development of nano-/micro-structural gradients.

Nature is especially adept in generating materials with unusual combinations of properties through the use of ingenious gradients, based on graded variations in local chemical composition,





**Figure 9.** Mechanical properties of the uniform grain-sized pure 30 nm nano-grained (NG) and pure 4–8  $\mu\text{m}$  coarse-grained CG structures, and the gradient structured (CG  $\rightarrow$  NG and NG  $\rightarrow$  CG) Ni at 293 K. (a) Uniaxial tensile properties of the NG structures exhibit a higher yield and ultimate tensile strength than that in the CG structures. A good combination of strength and ductility can be achieved in the gradient (GS) structure, as confirmed by its higher plastic work density (area under the true stress–plastic strain curve). (b) Crack-resistance  $R$ -curves for the four structures in terms of  $J$ -integral as a function of crack extension  $\Delta a$ . As the crack grows to  $\Delta a \sim 1$  mm, the  $J$ -based toughness value of the CG specimen is increased to  $442 \text{ kJ m}^{-2}$ , some six times higher than that of the NG sample,  $63 \text{ kJ m}^{-2}$ , showing evidence of ductile and brittle crack-growth behaviour in the CG and NG structures, respectively. The  $R$ -curve of the gradient NG  $\rightarrow$  CG structure shows higher slope than that of the pure NG structure as the crack grows into the gradient region, indicating an enhanced crack-growth toughness. The gradient CG  $\rightarrow$  NG structure displays a similar crack-resistance to the CG structure until the crack enters the nano-grained region where unstable fracture can occur [51]. (Online version in colour.)

constituents and structural characteristics involved in the arrangement, distribution, dimensions and orientations of the structural units [45]. For example, the mineralized collagen fibril structure of many fish scales, where the degree of mineralization in gradually decreased from the exterior of the scale to its interior, results in a hard outer surface to resist penetration from a predator attack but with a softer yet tougher interior to accommodate the excessive deformation [46]. Another pertinent example is bamboo, as its stems possess a graded structure comprising a decreasing density of vascular bundles from their exterior to the centre, resulting in enhanced flexibility yet overall strength and stiffness [47].

To mimic these structures, one common form of graded structures in synthetic materials has involved the use of gradients in grain size for metallic materials; indeed, several metallic materials with nano- to micro-scale grain-size gradients have been shown to achieve combinations of strength and ductility [48–51], although in most cases only in very small section sizes, often pertaining to a few hundred micrometres. Herein lies the current problem with this approach. Our processing capabilities to manipulate, at nano- to micro-scales, and fabricate such complex hierarchical and graded structures, i.e. from the ‘bottom-up’ like Nature, are still limited from the perspective of making macro-scale components; accordingly, currently, nano-/micro-scale graded materials have very limited application. To meet this challenge, however, three-dimensional printing and additive manufacturing techniques have the potential to make such complex bioinspired materials, although these techniques are still limited by the nanostructural dimensions that they can manipulate and in assuring the quality of the resulting material.

Recently, however, nominally bulk-sized graded metallic nickel has been processed as centimetre-sized plates by a direct-current electroplating process [50–52] to achieve grain-size gradients ranging from nanograins (NG) of approximately 30 nm to coarser grains (GC) of approximately 4–8  $\mu\text{m}$ . In addition to evaluating the role of gradients over larger dimensions, such larger-scale graded plates have permitted the assessment of their fracture properties as nano-/micro-sized samples can rarely satisfy the size requirements for realistic fracture toughness

measurement. With this objective, the mechanical properties of such gradient Ni under quasi-static loading have been assessed for the 30 nm to 4–8  $\mu\text{m}$  grain-size gradients (NG-GC), and compared to corresponding behaviour in uniform coarse (CG) and nanoscale (NG) grain-sized nickel [51]. By contrast to the NG and CG uniform grain-sized Ni, an optimized combination of high strength and toughness can be achieved in the gradient structured material, combining the higher strength of the nano-grained regions with the higher toughness of the coarse grains (figure 9). Interestingly, the fracture resistance of graded material is dependent on the crack direction, specifically due to the interaction of propagating cracks with the local microstructure within the gradient.

Using *J*-based *R*-curve measurements in the gradient materials (figure 9*b*), the crack-initiation toughness can be seen to be higher for cracks grown in the direction of the coarse-to-nano-grained (CG  $\rightarrow$  NG) gradient than vice versa, a result which can be ascribed primarily to crack-tip blunting in the coarse-grained microstructure [51]. Specifically, the CG  $\rightarrow$  NG structure displays the best combination of strength and toughness with the largest degree of crack-growth (*R*-curve) toughening, although at the end of gradient brittle fracture can occur within the nano-sized grains. The corresponding NG  $\rightarrow$  CG gradient structure exhibits lower crack-growth toughening but is actually less susceptible to outright fracture as cracks finally become arrested due to significant crack-tip blunting once they reach the coarser-grained regions. However, both gradient structures (CG  $\rightarrow$  NG and NG  $\rightarrow$  CG) display marked rising *R*-curve behaviour with exceptional  $K_{\text{I}}$ -based crack-growth toughnesses exceeding 200 MPa $\sqrt{\text{m}}$  at a tensile strength of over 1 GPa (figure 9) [51].

## 7. Concluding remarks

It is clear that the design of structural materials with enhanced damage tolerance and fracture resistance can be compromised by the problem that the properties of strength and toughness are often mutually exclusive. This is not so much of an issue with brittle materials that are extrinsically toughened as they develop fracture resistance by inducing crack-tip shielding, e.g. by crack deflection and bridging, to lessen the ‘driving force’ at a crack tip, but it certainly can be a problem in nominally ductile materials, which are primarily toughened intrinsically by plasticity or inelasticity mechanisms which resist damage created ahead of a crack tip. However, we have shown that through the occurrence of a synergy of deformation mechanisms which promote steady strain hardening (figure 8), or through the use of structural gradients (figure 9), that there are specific ways to ‘defeat’ the strength versus toughness ‘conflict’ in metallic materials.

We should note in passing here that there can be a downside to the extrinsic toughening of brittle materials. Although they are essentially not susceptible to fatigue, when they are extrinsically toughened they can become prone to premature failure under cyclic loading conditions [11]. A good example here is monolithic ceramics such as alumina, silicon nitride and silicon carbide which can be toughened by intergranular grain bridging; in fatigue, however, the frictional resistance of the grain boundaries is invariably diminished by continued sliding and wear due to the cyclic displacements such that the crack bridging, and hence the degree of extrinsic toughening, is progressively degraded [11]. This is one of the advantages of biological materials in that due to their multi-dimensional hierarchical structures, they can develop many different sources of toughening at different length-scales; accordingly, as illustrated by the example of bone in figure 2, natural materials are often toughened by both intrinsic and extrinsic processes. Moreover, because their architectures often comprise gradients in properties, composition, structural size and/or morphology, natural materials frequently exhibit desirable combinations of properties, again providing further ways to realize both strength and toughness.

Regardless of the strategy used, unlike untoughened brittle solids where unstable, often catastrophic, fracture ensues directly cracking is initiated, both the intrinsic and extrinsic modes of toughening serve to promote stable crack growth prior to outright fracture. It is the attainment of such crack-growth toughness, which is characterized not simply by crack-initiation parameters such as  $K_{\text{Ic}}$  but by the existence of rising crack-resistance or *R*-curve behaviour due to intrinsic



(plasticity) contributions and/or extrinsic toughening in the crack wake, which is the essential feature of strong and tough damage-tolerant materials and their resistance to fracture.

**Data accessibility.** This article has no additional data.

**Competing interests.** I have no competing interests to declare.

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