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Towards strength–ductility synergy through the design of heterogeneous nanostructures in metals

Evan Ma[a] **and Ting Zhu**[b,*]

[a] Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, USA
[b] Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

Metals can be processed to reach ultra-high strength, but usually at a drastic loss of ductility. Here, we review recent advances in overcoming this tradeoff, by purposely deploying heterogeneous nanostructures in an otherwise single-phase metal. Several structural designs are being explored, including bimodal, harmonic, lamellar, gradient, domain-dispersed, and hierarchical nanostructures. These seemingly distinct tactics share a unifying design principle in that the intentional structural heterogeneities induce non-homogeneous plastic deformation, and the nanometer-scale features dictate steep strain gradients, thereby enhancing strain hardening and consequently uniform tensile ductility at high flow stresses. Moreover, these heterogeneous nanostructures in metals play a role similar to multiple phases in complex alloys, functionally graded materials and composites, sharing common material design and mechanics principles. Our review advocates this broad vision to help guide future innovations towards a synergy between high strength and high ductility, through highlighting several recent designs as well as identifying outstanding challenges and opportunities.

Introduction

Metals are the workhorse material for the manufacturing industry and structural applications. This is largely because they have a good balance of strength and ductility. There is however a relentless quest to reach a more superior combination of strength and ductility. Unfortunately, these two properties are usually considered mutually exclusive: a gain in strength is inevitably accompanied by a sacrifice in ductility, resulting in a strength–ductility tradeoff [1–6]. For example, homogeneous nanocrystalline metals exhibit ultra-high strengths over 1 GPa, but that comes with diminishing (e.g., less than 5%) ductility (defined as the strain to failure in a uniaxial tension test) [7]. A major challenge, therefore, is to engineer novel microstructures to restore a respectable ductility to these high-strength metals, so as to achieve a desirable strength–ductility synergy [8,9].

There have been many success stories in the design of multicomponent and multiphase alloys [10,11], as well as composites [12,13], to achieve high strength while retaining reasonable ductility. The focus in this review is, however, on single-phase materials, such as elemental metals or solid solutions based on a primary element or on an intermediate phase. Elemental and single-phase metals are desirable in many applications. For instance, additional components or phases increase variables of processing and cost, make the material prone to corrosion due to inhomogeneities and associated disparity in electrochemical potentials, reduce the electrical and thermal conductivity, and bring in sites for stress concentration and crack initiation. Moreover, precipitation and dispersion of different phases require a delicate control of the phase decomposition sequence (e.g., to avoid over-aging in precipitation hardening).

In recent years, new material processing routes have emerged that enable microstructural control on the nanometer scale. One can now create heterogeneous nanostructures in an otherwise single-phase metal. The progress to be reviewed here has exploited this opportunity, through a common design strategy of heterogeneous nanostructured metals (HNMs). From this particular standpoint, the primary questions we aim to address are (i) what kind of nanostructure design in single-phase metals can push the boundary

**Corresponding author:*. Ma, E. (ema@jhu.edu), Zhu, T. (ting.zhu@me.gatech.edu)

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of the strength–ductility combination, and (ii) what are the new deformation mechanisms responsible for the enhanced strength–ductility synergy in these heterogeneous nanostructures. From both the materials science and mechanics perspectives, the principles and lessons learnt from these simpler single-phase materials can also shed light on the design strategies of overcoming the strength–ductility tradeoff for complex alloys and composites.

The strength–ductility tradeoff

Strength and ductility are among the most important mechanical properties of materials for structures and devices. Conventional coarse-grained metals have relatively low strength, but high tensile ductility. Homogeneous nanocrystalline metals with grain size finer than 100 nm usually exhibit more than five times higher strength than their coarse-grained counterparts [7,11]. This effect of ''smaller is stronger'' is generally understood in terms of the Hall–Petch effect of grain size strengthening. That is, grain boundaries can obstruct the motion of dislocations that serve as major carriers of plastic deformation at room temperature. As a result, the smaller the grains, the stronger resistances the grain boundaries provide against dislocation motion, and the higher the yield stress of plastic flow. In other words, the strength of polycrystalline metals can be increased by reducing the grain size. However, further reduction of grain size to less than about 20 nm could result in an effect of ''smaller is softer'', sometimes referred to as the inverse Hall–Petch effect [14–16]. Within the conventional Hall–Petch regime, one drawback with the size-strengthening approach is that the resulting materials suffer from greatly reduced ductility; the strain to failure is an order of magnitude smaller than that (often >50%) in coarse-grained counterparts. In particular, the uniform tensile strain before strain localization (necking) decreases to less than a few percent. The shaded area in Fig. 1 covers the typical experimental data of strength and ductility for various metals that have refined grains or dislocation structures, showing a fast loss of uniform tensile strain with increasing strength. Therefore, imparting high strength without conceding too much ductility is one of the major challenges in nanostructuring metals [17].

It should be emphasized that even a nanocrystalline metal is not intrinsically brittle due to the lack of plasticity mechanisms. For example, under a confined loading an electrodeposited Ni micropillar with 20 nm grain size can be compressed into a pancake (up to 200% true strain, or 85% reduction of its height) without fracture [26]. It is just that under high *tensile* stresses, the plastic elongation is susceptible to a localized necking deformation that instigates early failure. It is well known from the Hart criterion [27,28] that the necking instability sets in when

$$\frac{d\sigma}{d\epsilon} + m\sigma \leq \sigma \tag{1}$$

where σ is the true stress, ϵ is the true strain and m is the strain rate sensitivity. Since m is not sufficiently high in nanostructured metals ($m < 0.05$ at room temperature) [29–32], the strain-hardening rate $d\sigma/d\epsilon$ (i.e., the tangent slope of the true stress–strain curve in Fig. 2) has to be high enough to keep up with the increasing stress σ for averting the inequality in Eq. (1), so as to stabilize the uniform tensile plastic deformation. Incidentally, achieving a high tensile ductility resulting from enhanced stable plastic flow

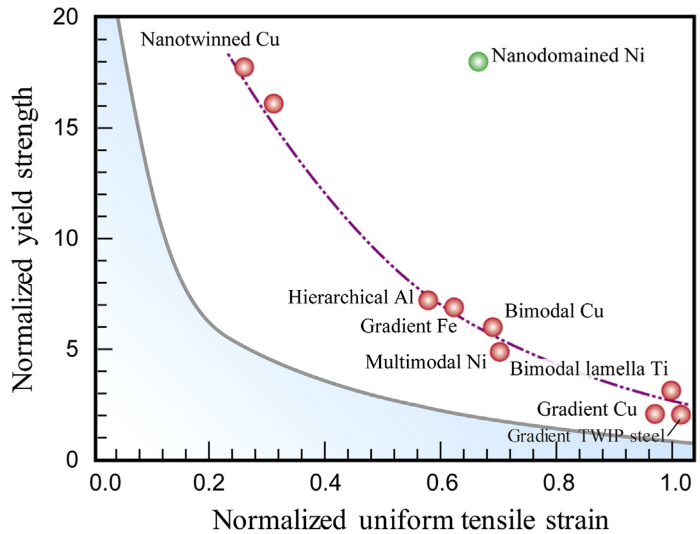

FIGURE 1

Yield strength versus uniform tensile strain of metals. For each material, the strength and ductility are normalized, with the reference being the engineering yield stress and uniform tensile strain of the coarse-grained counterpart, respectively. The shaded area under the banana-shaped curve covers the strength–ductility data of conventional metals with homogeneous nanostructures. The reader is referred to the literature [2,18,19] for numerous data points already summarized previously. The solid circles along the dashed line (a guide to the eye) are HNM examples cited in the text with an elevated combination of strength and ductility; from left to right: nanotwinned Cu [19], hierarchical Al [20], gradient Fe [21], bimodal Cu [2], multimodal Ni [22], gradient Cu [23], bimodal lamella Ti [24], gradient TWIP steel [25] and nanodomained Ni [18]. The hierarchical Al [20] had the composition of a 7075 Al alloy, but was made into a *single-phase* FCC solid solution via severe plastic deformation; so comparison was made with reference to a solution-treated but un-aged bulk metastable single-phase alloy at this composition. Here, the normalized strength and ductility values quantify the change in properties, i.e., the improvement with respect to their coarse-grained counterpart as the reference.

can be beneficial for improving fracture toughness [33], despite the different stress states under uniaxial tension and at the crack tip.

For almost all metals after strengthening such as cold working or grain refinement, the slope of the stress–strain curve in the plastic flow regime (i.e., strain hardening modulus) is much lower than for coarse-grained metals [29,34]. For example, in nanocrystalline grains with abundant high-angle grain boundaries, almost all the dislocations mediating the plastic strain would quickly traverse the tiny crystal grains, and annihilate into the surrounding grain boundaries, with little chance and space to be retained inside [34]. Molecular dynamics simulations also indicate that the grain boundary pinning structures can be altered by absorbed dislocations, thus changing the strengthening effect of the grain boundary pinning content [35]. These processes take away an effective strain hardening mechanism in coarse-grained metals, i.e., the continuous multiplication and storage of dislocations during plastic straining. Consequently, $d\sigma/d\epsilon$ is typically low, leading to an early necking instability at a low tensile strain, especially when compounded by a high tensile stress. As shown in Fig. 2 using homogenously-grained Ni with different grain sizes as an example, increasing the yield strength (by decreasing grain size) leads to a fast drop of the uniform tensile strain, all the way to the nanocrystalline case (18 nm) where the tensile ductility almost vanishes. This example further demonstrates the

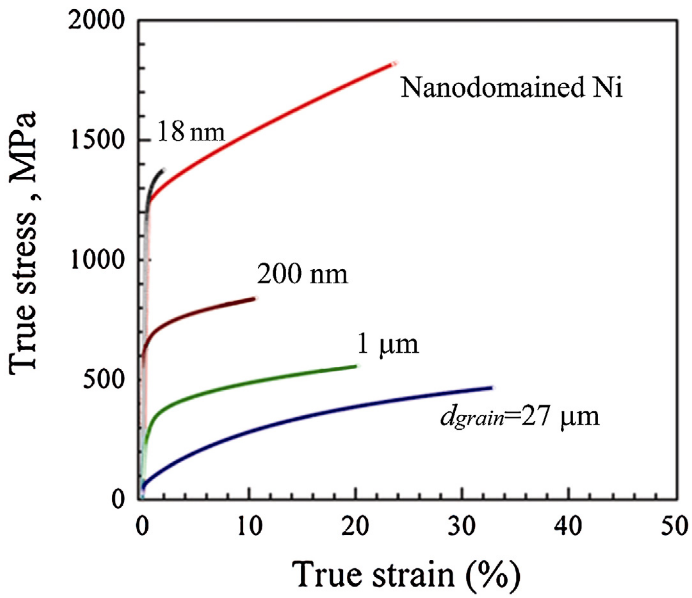

FIGURE 2

Tensile stress–strain curves of Ni [18]. The coarse-grained Ni has an average grain size d of 27 µm. Other electrodeposited Ni samples have d ranging from 1 µm to 18 nm. The nanodomained Ni contains domains with an average size of 7 nm and small misorientations (<15°) with the matrix (see detailed description associated with Fig. 3f). The true stress–strain curves are converted from engineering stress–strain curves (up to the maximum stress point where non-uniform elongation sets in).

strength–ductility tradeoff shown in Fig. 1. The exceptional case of nanodomained Ni will be discussed next.

Heterogeneous nanostructured metals

A high strain hardening capability is therefore key to evading the strength–ductility tradeoff. In this regard, creation of heterogeneous nanostructures is particularly beneficial and has therefore served as an overarching mechanism in promoting strength–ductility synergy. In heterogeneous structures, soft and hard regions (e.g., small and large grains) are mixed together. Soft regions deform plastically more than hard regions, so that gradients of plastic deformation build up. Accommodation of such plastic gradients requires the storage of geometrically necessary dislocations [36] (dislocations of same sign), which contribute to work hardening. This is a non-local effect of strengthening. The characteristic length scale of gradient plastic deformation, λ, is determined by the spacing between neighboring soft and hard regions. It was pointed out by Ashby [36] long time ago that the density of geometrically necessary dislocations is proportional to local plastic strain but inversely proportional to λ. Heterogeneous nanostructures are characterized by unusually small λ, and thus offer a high capacity of storing more geometrically necessary dislocations, thereby enhancing the strain hardening and consequently strength–ductility synergy. This key message will be emphasized time and again in this review, for HNMs that are plastically non-homogeneous [36] with large strain gradients.

Thermomechanical routes for preparing heterogeneous microstructures normally involve severe plastic deformation [3,4,38] and dynamic plastic deformation [39,40], followed by an annealing treatment. The resulting materials usually have complicated residual deformation microstructures as well as a strong deformation texture. With the newly acquired ability to control structures on the nanometer scale via either a top-down or a bottom-up approach, one can now purposely deploy heterogeneous nanostructures in an otherwise single-phase metal. In the following we provide a review on several representative designs of HNMs employing bimodal, harmonic, lamellar, gradient, domain-dispersed, and hierarchical nanostructures.

Bimodal grains

Wang et al. developed a thermomechanical processing route to obtain a bimodal distribution of grain size in Cu [2], with 25 vol% micrometer-sized grains randomly embedded among ultrafine (<200 nm) grains (Fig. 3a). Cryogenic rolling was applied and then followed by secondary recrystallization during which new grains grew abnormally at the expense of others to reduce surface area. The resulting sample with bimodal grains retained a high strain hardening rate as coarse-grained counterparts. More discussions about the design and processing issues pertaining to this strategy will be presented in the next section. The extra work hardening capacity of bimodal grains was attributed to dislocation accumulation arising from ''an excessively large number of geometrically necessary dislocations that form to accommodate the large strain gradient across the ultrafine-coarse grain boundaries'' [2]. This work has motivated explorations on various other derivatives of bimodal grains, such as those with a harmonic structure and a heterogeneous lamella structure to be reviewed next, as well as other multimodal grain distributions [11,22,41].

Harmonic structure

Ameyama and co-workers proposed a design concept of bimodal grains with a 'harmonic structure' [37,42,43]. The key idea is the creation of a continuous three-dimensional network of hard ultra-fine-grained skeleton filled with islands of soft coarse-grained regions. The 'harmonic structure' of bimodal grains was fabricated by a two-step process: they first applied severe plastic deformation to micron-sized powders with coarse grains through mechanical milling or high-energy ball milling, so as to create a ultrafine-grained shell; and then they used spark plasma sintering or hot roll sintering to consolidate powders. The resulting harmonic structure has almost null porosity, while preserving the heterogeneous structure. This approach enables a control of both the topology of ultra-fine grained skeleton and the scale of the structural heterogeneity in bulk samples. Recently, Sawangrat et al. fabricated Cu samples with such a 'harmonic structure' of bimodal grains (Fig. 3b) [37]. The associated mechanical testing showed a favorable combination of high strength and large elongation superior to its homogeneous as well as bimodal heterogeneous counterparts. Unique features of harmonic structure, i.e., continuous network of ultra-fine grained regions encompassing coarse-grained areas, led to the extension of uniform tensile strain. The optimum combination of properties in pure Cu was found to be in the harmonic-structured material having 40% ultra-fined grains.

Heterogeneous lamella structure

Wu et al. developed a heterogeneous structure of bimodal grains in Ti [24], which features soft micro-grained lamellae embedded in a hard ultrafine-grained lamella matrix (Fig. 3c). They produced this heterogeneous lamella structure by asymmetric rolling and partial

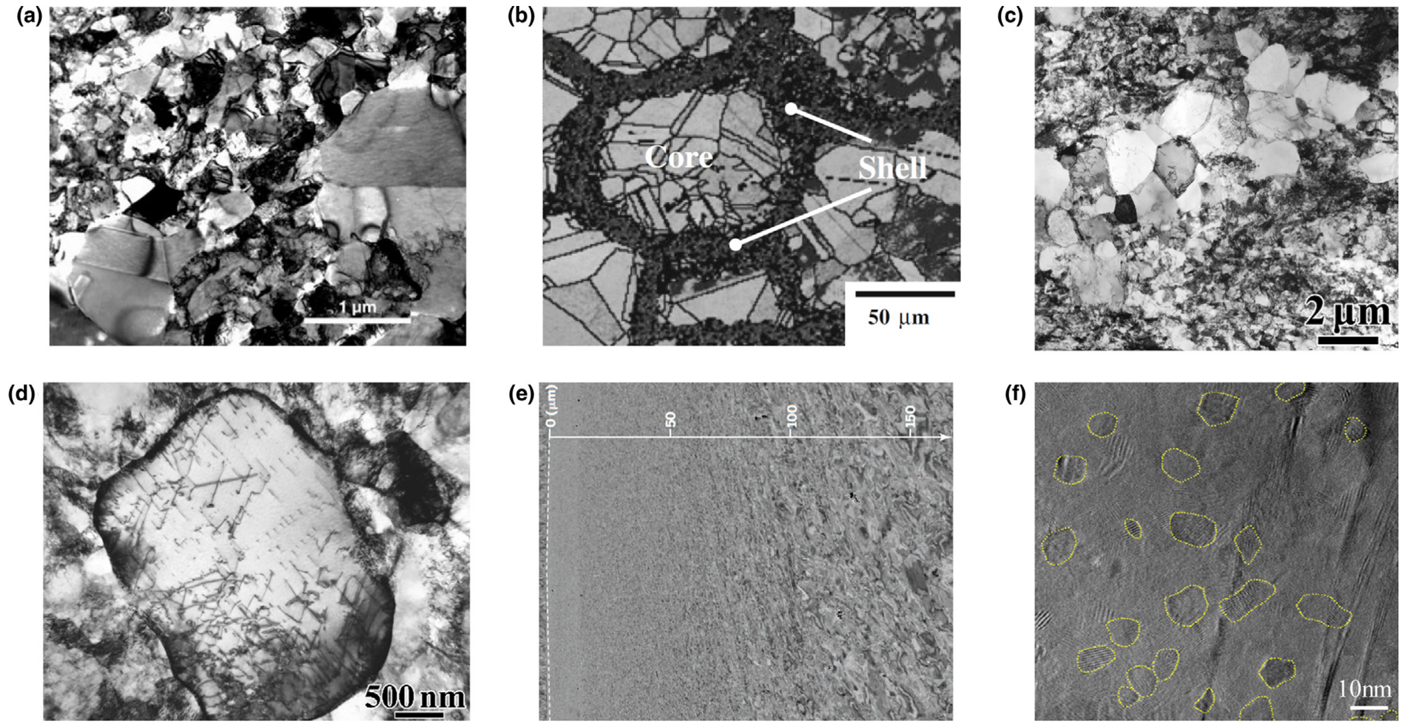

FIGURE 3

Examples of heterogeneous nanostructured metals. (a) Transmission electron microscopy (TEM) image of Cu with bimodal grains, showing 25 vol% micrometer-sized grains randomly embedded among ultrafine (<200 nm) grains [2]. (b) Electron back scattering diffraction (EBSD) image quality map overlaid with grain boundaries in the cross section of a bimodal grained Cu sample with a 'harmonic structure' [37]; it was produced by consolidation of powders with a core–shell microstructure wherein the coarse-grained inner part of the powder is surrounded by a severely deformed layer with submicron sized grains. (c) TEM image of Ti with heterogeneous lamella structure, showing a lamella of recrystallized grains in between two lamellae of ultra-fine grains [24]. (d) TEM image showing the buildup of a high density of dislocations at several locations in a large grain surrounded by small grains in a deformed Ti with heterogeneous lamella structure [24]. (e) Scanning electron microscopy (SEM) image of gradient nano-grained Cu with a gradual gradient in grain size from the surface to interior [8]. (f) TEM image of nanodomained Ni, showing the distributed nanoscale Ni domains of about 7 nm in size and small misorientation (<15°) with the Ni matrix crystal [18]. Overall, the heterogeneous nanostructures in (a–d, f) have in common a bimodal size distribution, but involve different spatial arrangements and/or shapes of nanostructures. In contrast, the heterogeneous nanostructure in (e) represents a different class of multimodal size distribution and features a gradient (layered) variation of grain size in this case.

recrystallization. The resulting material is as strong as ultrafine-grained Ti and at the same time as ductile as conventional coarse-grained Ti. A major revelation came from their loading–unloading–reloading tests: during unloading, reverse plastic yielding starts even when the applied stress is still in tension, and the resulting stress–strain hysteresis loop reveals a back stress as large as 600 MPa. The strain partitioning analysis indicates that the soft coarse-grained lamellae carry much more plastic strains than the surrounding hard regions. Many geometrically necessary dislocations accumulate in the soft, large grains near the interfaces against the hard, ultrafine-grained lamellae (Fig. 3d). The storage of geometrically necessary dislocations with increasing load was considered to be responsible for the buildup of long-range back stresses. Such back stresses resist forward dislocation motion and assist reverse glide, leading to a low yield stress when the loading is reversed. This is known as the Bauschinger effect [44]. As such, this work demonstrates a prevalent kinematic hardening effect in heterogeneous nanostructures.

Gradient grains

At another front of research for controlling the grain size distribution, a spatial gradient in grain size can be produced in the surface layer of a metal, giving rise to ''gradient nano-grained metals''. Incidentally, materials with spatial gradients in composition and structure near surface has been of considerable interest in the field of tribology for enhancing resistance to contact deformation and damage [45]. To produce nanostructures on the surface of bulk coarse-grained metals, various surface plastic deformation techniques have been developed, such as surface mechanical attrition treatment (SMAT) and surface mechanical grinding treatment (SMGT) [46–48]. In a recent study, Fang et al. used SMGT to process a gradient nano-grained layer enclosing a coarse-grained core of Cu [23]. As shown in Fig. 3e, the topmost layer of the gradient structure, up to a depth of 60 µm, consists of nano-grains with an average grain size of about 20 nm. The grain size gradually increases to about 300 nm in the depth of 60–150 µm. Below a depth of 150 µm, the grain size continues to increase to that of coarse grains at the micrometer scale. The gradient nano-grained layer exhibits a high yield strength, and when constrained by the substrate can sustain a tensile true strain exceeding 100% without cracking. Another example is that of Wu et al., who used SMAT to prepare the gradient nano-grained steel with a sandwich sheet structure, i.e., a coarse-grained core in between two surface gradient nano-grained layers [21]. The tensile tests showed that the gradient structure induces an extra strain hardening and hence high ductility. This extra strain hardening was attributed to the buildup of geometrically necessary dislocations, as well as to the multiaxial stress states arising from interplay between the coarse- and fine-grained sub-layers that promotes the activation of new slip systems and dislocation accumulation. Several examples of such gradient nano-grained metals are included in Fig. 1. It should be noted that to date, most gradient nano-grained structures have been made on the surface of a coarse-grained substrate, graduated with a smooth gradient of grain size. The processing relies on surface mechanical treatment that limits the thickness of the near-surface, gradient nano-grained layer. As a result, the strength–ductility synergy in the entire sample is limited. Further development in this direction thus calls for new processing routes to reduce the ratio of the thickness of the bulk sample to its hardened surface layer of gradient nano-grains. Very recently, Thevamaran et al. reported a dynamic creation of gradient nano-grained structures in single crystal silver microcubes undergoing high-velocity impact against an impenetrable substrate [49]. Their work demonstrated a promising pathway to develop the gradient nano-grained metals with a large gradient in grain size ($\sim$1), which is at least one order of magnitude higher than that produced by SMAT and SMGT.

Dispersed nanodomains

Wu et al. reported the processing of a novel class of heterogeneous nanostructures that involves ''self-dispersion strengthening without the second phase'' in Ni [18]. They developed a pulse electroplating protocol to deploy nanoscale Ni domains that are single crystals with small misorientations ($<15^{\circ}$) with the matrix crystal. These nanodomains occupy less than 3% of the total volume. They are about 7 nanometers in diameter, but numerous in population (hence closely spaced) and spread out in the much coarser Ni grains (Fig. 3f). Three desirable features of high strength, high strain hardening rate and high ductility are realized simultaneously. The yield strength of this nanodomained Ni is on par with that of nanocrystalline Ni composed of equi-axed grains of 18 nm (Fig. 2) [34]. This has been attributed primarily to the small spacing between nanodomains that effectively increases the pinning resistances to dislocations in the matrix. In addition, the pinning/depinning actions result in sluggish dislocation motion and provide more chances for dislocations to run into each other, interact and multiply, elevating the storage rate of dislocations in the grain volume. These factors can be responsible for the high strain hardening rate in the true-stress–strain curve in Fig. 2, where the slope is even higher than that of coarse-grained Ni (compare the red and blue curves). The pronounced strain hardening promotes the uniform elongation to approach that of coarse-grained Ni. Previously at such a uniform elongation, the banana curve or even the dashed purple line in Fig. 1 would predict a strength nowhere close to the GPa level seen for the red curve in Fig. 2. With the abundant domain boundaries containing concentrated dislocations and their sources, the effective dislocation density in the material is very high, such that a high strength is achieved. Each group of dislocations is already organized into a relatively low-energy configuration in a discrete domain boundary, such that even low-angle boundaries remain fairly stable during deformation and sample storage, at least for the impurity level typical of electrodeposits [18]. The system of ''Ni nanodomains inside coarse-grained Ni'' is an exceptional case in the strength–ductility space. While the required structural control on the nanometer scale is challenging to attain in general, this system lends support to the following perspective: for maximizing the strength–ductility synergy a heterogeneous nanostructure should be designed to best serve the dual purpose of blocking and accumulating dislocations: the dislocation barriers need to be created not only to provide plentiful roadblocks, but also positioned to leave ample space to allow for the multiplying dislocations to accumulate [18,50,51].

Hierarchically structured grains and twins

In addition to tailoring the grain size and distribution in general, one can create a hierarchical structure with a combination of heterogeneous grains and nanostructures characterized by other types of special grain boundaries, such as twin lamellae with coherent twin boundaries or nanolaminates with low-angle boundaries. In metals with low stacking fault energies such as Cu and Ag, nanoscale twin lamellae can form during either growth or deformation processes. Twin boundary is a coherent and stable interface that can strongly obstruct slip transfer of dislocations [19,52–57]. As a result, the presence of a high density of twin boundaries (e.g., nanoscale twin lamellae in ultrafine grains) changes the dislocation glide behavior, resulting in the hard and soft modes of slip [58,59]. In the hard mode, dislocations glide on the slip systems inclined to the twin boundary and are thus constrained by the small twin spacing. In the soft mode, dislocations travel parallel to the twin boundary and thus experience less resistances from twin boundaries. Lu et al. produced a nanotwinned Cu system where uniformly large grains in the micrometer range contain a high density of twin lamellae with the thicknesses of a few tens of nanometers [19]. Such nanotwinned Cu exhibited an ultrahigh tensile strength about 10 times higher than that of conventional coarse-grained Cu, while retaining a decent tensile ductility.

It naturally follows that one can build a hierarchical microstructure combining heterogeneous grains and twins [25]. Along this line of thinking, Lu [60] has recently discussed several possible designs, including gradient grains with uniform nanotwins, gradient nanotwins in homogeneous grains, and concurrent gradients in grains and twins (i.e., small grains contain thin twins, while large grains thick twins). Optimizing such hierarchical grains and twins for a better synergy of strength and ductility calls for new advances in the processing techniques for nanostructure control. Moreover, we note that in metals with high stacking fault energies, such as Ni and Al, twin boundaries are difficult to form. But low-angle grain boundaries are routinely formed by dislocation multiplication and interaction through plastic deformation [61]. These low-angle boundaries can play a role similar to twin boundaries and general high-angle boundaries for impeding dislocation motion [28]. Hence, it would be interesting to compare the designs of hierarchical Cu and Ni for a better understanding and rationalization of the synergistic effects of different combinations of heterogeneous boundary structures. Also possible is another type of hierarchical nanostructure featuring solute-enriched regions rather than grains alone, as shown for the case of an Al alloy [20], where $\sim$10 nm sized solute-aggregated clusters are spread heterogeneously in multiple locations, including the grain interior as well as the grain boundaries and their junctions. The material actually had the composition of a 7075 Al alloy, but was made into a *single-phase* face-centered-cubic solid solution via severe plastic deformation. The combination of strength–ductility was much improved relative to unaged coarse-grained alloy at this composition.

Examples of the above sub-groups of HNMs are marked in Fig. 1. These variations have all improved the strength–ductility combination to various degrees, at a new level (e.g., those along the dashed purple line) obviously elevated from that of conventional homogeneous microstructure (shaded area under the banana curve).

Materials design considerations

The common thread underlying the different HNMs as reviewed above is the paradigm of tailoring nanostructural heterogeneity for a synergy of strength and ductility. Heterogeneity can be in a variety of shape and form, taking different size and spatial distributions of the constituent grains, in concert with their morphological features such as lamellae, domains, or graded layers. There are outstanding challenges in designing and manufacturing these inhomogeneous microstructures, as well as in understanding the structure-property relations. In this section, we discuss several common materials science issues as well as their mechanics ramifications. The problems discussed here also suggest that opportunities abound in the emerging area of designing heterogonous nanostructures, in order to achieve a better strength–ductility synergy for accessing the unoccupied space in Fig. 1 (e.g., around the green point). These tasks are likely to be active research topics for years to come. Design and processing choices should be made intelligently depending on the properties sought after and the processing tools at hand.

In comparison, engineering alloys and composites are inherently heterogeneous, and their plastic deformation has been extensively studied [36]. When it comes to making single-phase HNMs, the primary task is to rationally design and engineer heterogeneities at the nanoscale, now without the inclusion of foreign phases. This brings forth hitherto unheralded ingredients and opportunities to reap the benefits of composite engineering, but also presents challenges.

Processing

During materials design and processing, one needs to control and optimize not only the volume fraction, but also the morphology and topology, of the heterogeneities, as all of these variables might strongly influence the properties. The grain size distribution, spatial variation (e.g., constant gradient, varying gradient, random gradient, magnitude of gradient), and morphology (lamellae, domains, aggregates, percolation, etc.) can all be inter-related design parameters that change mechanical properties. To control these factors in bulk samples, it is necessary but challenging to invent novel processing methods (e.g., gradient is often produced by surface treatment but that limits the depth affected to less than a small fraction of one millimeter). In this regard, the heterogeneities add considerable complexity to processing. It is non-trivial to design the structures *a priori*, and then produce them by experiments as planned. Because of the wide range of multiple variables, it is also a major challenge to reach the designed structures reproducibly. In addition, it remains little known how to maintain the heterogeneous nanostructures during long-term applications of HNMs, particularly at elevated temperatures. On the bright side, there are many parameters as knobs to turn for achieving the optimal strength–ductility combination. It is worth noting that such heterogeneous microstructures are the prominent feature in materials processed by additive manufacturing [62], which enables the building of three-dimensional (3D) objects by adding material layer-upon-layer, via for example spreading and selectively melting individual powder layers. While the required heterogeneity control on the nanometer scale is challenging to additive manufacturing at present, it may very well become easy in the near future, considering fast and continuous advances in novel additive manufacturing processing [63,64]. In the short term, the spark plasma sintering is a more feasible method for preparing designer HNMs by consolidating powders under a relatively low pressure while being heated through the application of a pulsed direct current [65]. This method has been used to form metal samples with a fine grain size in near-micrometer regime [66]. Recent development allows for the sintering of metal powders of different sizes for creating bulk samples with a bimodal and even a multimodal distribution of grain sizes [67].

At the front of microstructure characterization, digital representation tools for the analysis of microstructure in 3D are being rapidly developed, thanks to recent efforts on Integrated Computational Materials Engineering (ICME) and the Materials Genome Initiative (MGI) [68]. As a result, the software such as DREAM.3D provides a powerful environment for processing, quantifying, representing and manipulating the digital microstructure data taken from serial sections of a polycrystalline sample by electron back scattering diffraction [69]. Such high-fidelity tools enable the 3D quantitative characterization of internal heterogeneous microstructures. The digitally reconstructed microstructure can be used for further analysis by microstructure sensitive computational models [70,71]. Another recent development of the digital representation tool is NEPER which provides a software environment for polycrystal generation and meshing [72]. It can be adapted to build models of heterogeneous grains with controllable sizes and distributions. Fig. 4 shows examples of heterogeneous grains with a bimodal versus a multimodal distribution of grain sizes. We expect that a close integration of novel visualization techniques

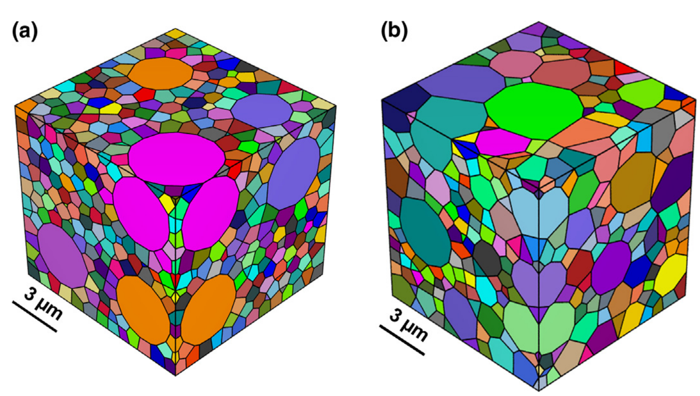

FIGURE 4

Structure models of heterogeneous grains with controllable grain size and distribution. (a) A bimodal grained structure with ~50 vol% grains of size of 1 μm and 50 vol% grains of 6 μm. (b) A trans-modal grained structure with a uniform distribution of grain sizes in between 1 μm and 6 μm. Grain is colored according to its orientation assigned randomly.

with material processing would provide a transformative approach for the creation of designer HNMs towards unprecedented strength–ductility synergy.

Deformation mechanisms

From the materials science perspective, in these HNMs an extra materials strengthening mechanism arises from the intentionally introduced heterogeneities, because the latter promote the accumulation of dislocations and dictate their distribution. Specifically, geometrically necessary dislocations will build up to accommodate the deformation incompatibility near grain boundaries, domain boundaries and interfaces separating the soft and hard regions. These accumulated dislocations, on one hand, directly contribute to strength and ductility through forest hardening and cross-slip mechanisms, and on the other hand, generate long-range stresses impeding dislocation motion in regions away from interfaces and thus cause additional hardening. In other words, besides the average dislocation density, the distribution of dislocations (i.e., density gradient) makes an extra difference in hardening. This should be common to all the HNMs. But for each type of HNMs, the dislocation distribution underlying the inhomogeneous plastic strain would vary, and this is expected to produce a non-local strengthening effect to different degrees. A gradient of grain sizes would produce a corresponding gradient in geometrically necessary dislocations, since their density would depend on the size of the grains [36]. The largest local dislocation density gradients would result, in the case of randomly dispersed large grains that are fully embedded within surrounding small hard grains. It remains unclear which type and form (gradient, lamellae, aggregated domains, uniform versus random distribution, etc.) is more efficient and effective in sustaining strain hardening. To address these questions, real-time characterization techniques [73–80] such as in situ transmission electron microscopy and synchrotron X-ray diffraction can be utilized to reveal how the interplay of geometrically necessary dislocations and heterogonous nanostructures affects the strength, hardening and ductility properties of HNMs.

Fig. 1 displays the best HNM examples thus far: they suggest strength–ductility combinations superior to the weighted average given by the rule of mixtures based on the volume fraction of constituent grains, in stark contrast to the shaded area for conventional microstructure (see Fig. 1). But there are also bimodal and multimodal cases where the resulting strength–ductility combination remained below the rule-of-mixtures average. The outcome is apparently rather sensitive to the various details mentioned above [11]. This remains poorly understood at present. In general, there is a lack of quantitative explanation to, let alone an *a priori* prediction of, the measured strength–ductility. Innovative experiments and modeling are needed in a visionary design of the heterogeneous microstructure that can optimize the properties and predict their ultimate limits reachable in future [11]. In addition, the mechanisms governing the thermo-mechanical stability [9,81,82] of heterogeneous nanostructures must be understood and controlled for effective processing and utilization of HNMs.

Mechanics

Understanding and quantifying the mechanics of inhomogeneous plastic deformation is pivotal for a rational design of HNMs. In an HNM under a macroscopically uniform load, there will be load redistribution and strain partitioning among different soft and hard regions (e.g. grains). This arises due to progressive yielding of the different sized grains that have different yield strengths and strain hardening capacities. Near the yield point, a transient of gradual elasto-plastic transition arises, giving rise to apparent strain hardening [83]. The strain inhomogeneity creates inhomogeneous internal stresses such as long-range back stresses, in addition to the strengthening generated by local plastic strains. Such back stresses are strain dependent and strain path dependent, leading to the Bauschinger effect and kinematic hardening, on top of the short-range forces required to cut through the forest dislocations statistically stored inside the grains that contribute to isotropic hardening. Note that the general idea of ‘‘promoting dislocation storage for strain hardening’’ discussed in the context of Eq. (1) points to the same effect and remains the general strategy, because a high density of stored dislocations in these HNMs usually also implies that geometrically necessary dislocations would be populous and strain gradients would be large, such that the internal stresses would be high. For HNMs, the first term (the hardening modulus) of the left-hand side of Eq. (1) can be decomposed into multiple terms, reflecting the specific contributions from forest dislocations stored in the grain interior and particularly from the non-local strengthening of geometrically necessary dislocations and other piled-up dislocations, respectively. The notion of non-local strengthening is consistent with that in the widely studied strain-gradient plasticity [84–86], but the difference is that back then the strain gradient was considered to be induced by imposing a non-uniform deformation, such as torsion, bending and indentation [84–86], on an otherwise homogeneous microstructure. With HNMs, it is the heterogeneous microstructure that makes the material plastically non-homogeneous, for enhancing the strain hardening rate with the increase of overall plastic strain in the sample. For example, it is known that there is an obvious up-turn of the strain hardening rate along with the transient after an apparent yield point; during this transient gradually all the grains accomplish the elasto-plastic transition [87].

In addition, another significant mechanics effect is that the presence of plastic strain gradients can induce multiaxial stress states under uniaxial loading conditions. This arises due to interplay between the coarse- and fine-grained regions/layers for accommodating the strain incompatibilities. As an important consequence, the multiaxial stresses can promote the activation of new slip systems and dislocation accumulation [21].

The above analysis of the mechanics of inhomogeneous plastic deformation and associated gradient plasticity can be understood using gradient nano-grained Cu, as an example of HNMs. The simplified composite models [88–90] assume a one-dimensional spatial gradient in grain size from the surface to the bulk interior and employ the grain size-dependent plasticity relation to shed light on the general mechanics response of a broader class of HNMs. It is relatively easy to obtain such a gradient microstructure in experiment (e.g., by SMAT or SMGT), and the gradual grain size distribution is amenable to modeling. Recently, Zeng et al. developed a grain size dependent crystal plasticity finite element model to investigate the spatial-temporal evolution of gradient stress and strains [83]. A plastic strain gradient is clearly observed in Fig. 5a.

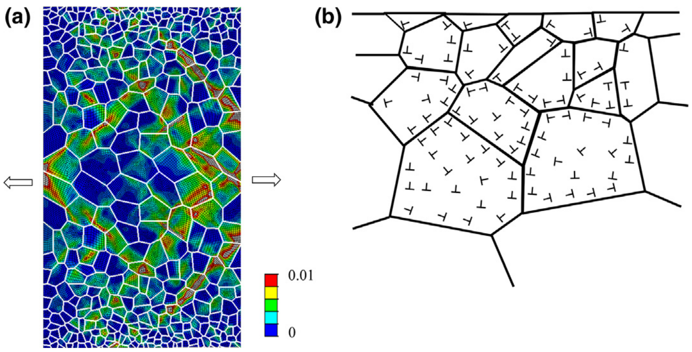

FIGURE 5

Modeling of plastic strain gradients imposed by gradient nano-grains in Cu [83]. (a) A finite element crystal plasticity model of quasi-two-dimensional structure of columnar nano-grains was constructed with a continuous spatial gradient of grain sizes linearly varying from ~20 nm in the top/bottom surface layer to ~110 nm in the central region. The sample is pulled under axial tension along the horizontal direction under the plane strain condition. Contour of axial plastic strains at an applied strain load of 0.5% shows the distribution of gradient plastic strains. Grain-size-dependent yield strength was taken into account in the crystal plasticity model. (b) Schematic illustration of a gradient variation of the density of geometrically necessary dislocations (represented by ⊥ near grain boundaries) in a gradient nano-grained structure.

Correspondingly there will be a gradient in the density of geometrically necessary dislocations, as illustrated in Fig. 5b. This is because accommodation of deformation incompatibility between adjoining grains requires the generation of geometrically necessary dislocations near grain boundaries, whose density depends on both the gradient grain size and resulting gradient plastic strains. The model reveals progressive yielding, with the larger and inhomogeneous strains in the central region, and smaller inhomogeneous strains in the top/bottom surface layers. Such plastically inhomogeneous deformation is known to provide a non-local effect of material strengthening [36]. Again, the latter has long been recognized in the gradient plasticity theory [84–86], under non-homogenous deformation. The new application of the gradient theory to internal heterogeneities responding to an overall uniform deformation requires a systematic and quantitative study in future, via further development of non-local plasticity model and associated numerical procedures.

Conclusion and outlook

The design concept advocated in this review follows a general mechanical metallurgy principle: to retain ductility the microstructure should be engineered to delocalize strain concentration and encourage a spread-out distribution of plastic flow. In particular, to stabilize uniform tensile elongation an adequate strain hardening (and/or strain rate hardening) capability must be present. Our thesis is that baring additional reinforcing/ductilizing phases, there are still multiple facets of structural inhomogeneities that can be invoked and tailored to accomplish this goal in an otherwise single-phase material. These messages have been illustrated using recent examples, under a common umbrella of heterogeneous nanostructured metals. These HNMs can accomplish what is achieved by non-local hardening effects in dual-phase alloys and composites with multiple components. Incidentally, even for submicron pillars and nanopillars, non-local hardening and the Bauschinger effect have also been invoked recently to simultaneously improve the strength and the stability against strain bursts, by passivating or coating the pillar surface or introducing second-phase precipitates [91–94]. The principles underlying such familiar practices in complex materials can now be adopted for single-phase materials: purposely engineered inhomogeneities become the intended microstructure, in lieu of the uniform microstructure traditionally thought to be preferable in metals. In these otherwise homogeneous metals perhaps the most convenient microstructural heterogeneity is in the form of transmodal grain/twin sizes and their spatial distribution (e.g., Fig. 4b), which can then be judiciously manipulated at the nanometer scale, and hopefully custom-designed in future, to ward off plastic instabilities [95] and realize a desirable strength–ductility combination.

Examples of heterogeneous nanostructured metals spread over various materials research communities, including those working on nano- and ultrafine-structured metals, laminated or functionally graded materials, gradient nano-grained metals, hierarchical and architected materials, small-volume materials (e.g., micropillars), and thermomechanical processing of bulk metals. In general, pronounced non-local strengthening follows from the development of non-homogeneous plastic deformation due to intentionally embedded microstructural inhomogeneities, contributing to strength and strain hardening especially when the structural/strain gradient is large. Structural heterogeneity can also mimic the well-known Orowan strengthening in precipitation hardened alloys [96,97]: a small volume fraction of dispersed nanodomains [18] can already impart GPa strength; it reaps the benefits of nanostructured boundary hardening in the absence of contiguous nanocrystalline grains, and of precipitation/dispersion hardening but without GP zones [98] and a second phase [50]. A major advantage of these heterogeneous nanostructures over the conventional homogeneous and contiguous nano-grains [94,99] is the possibly increased opportunities for dislocations to stall, multiply and accumulate, sustaining a strain hardening rate in excess of that of coarse-grained counterpart and a uniform elongation previously unexpected for high-strength metals. There is clearly a need for detailed understanding of these mechanistic processes so as to develop effective means to promote the strength–ductility synergy in heterogeneous nanostructured metals.

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