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Stability of nanocrystalline metals: The role of grain-boundary chemistry and structure

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Nanocrystalline metals are transitioning from laboratory curiosities to engineering materials, in large part due to advances in improving their stability, making their exceptional properties more predictable and accessible. Nanoscale grains typically have a very strong innate tendency to coarsen, but the grain-boundary structure can be designed and tuned to lower its excess energy, reducing both the driving force for coarsening and the grain-boundary mobility. This article reviews two major strategies for achieving low-energy grain boundaries in nanocrystalline structures. First, grain-boundary alloying is discussed, including grain-boundary segregation and its energetic competition with the formation of second phases; with sufficient grain-boundary segregation tendency it is possible to stabilize nanostructures to high temperatures. Second, methods of achieving low-energy crystallographic grain-boundary structures are discussed, including the formation of nano-twinned structures and relaxing grain boundaries into low-energy structures through their interactions with partial dislocations. Both of these strategies have led to effective and implementable stable nanocrystalline materials, and point to many directions for future advancements.

Keywords: nanostructure, grain boundaries, alloy, twins

Introduction

Research on nanocrystalline materials over the past several decades has followed a trajectory of increasing stability. The first nanocrystalline materials were produced using exotic, far-from-equilibrium processes such as condensation from inert gases, [1,2] and were so unstable that they could not be produced at full density without triggering grain growth that threatened their nanostructure. Subsequent work on severe plastic deformation of pure metals [3] led to significant advances in achieving full-density material with fine grain sizes, and electrodeposition achieved

even ~10–20 nm grains in some pure metals. [4,5] However, it was subsequently realized that these materials were also unstable against grain growth: grains would grow at low homologous temperatures as low as ~0.2 T_m (with T_m the melting point), even at room temperature. [6,7] Abnormal grain growth was also often found to occur with a few grains rapidly expanding to the micron scale. [7]

Although many of these early experimental nanocrystalline materials were unstable, work on them substantially increased our understanding of their exceptional properties: enhanced strength, [1,8–10] hardness, [11–14] wear, [9,15,16] magnetic properties, [17–21] thermoelectricity, [22–31] and others. [32–46] They established a strong value proposition driving further interest in nanocrystalline materials for a variety of engineering applications. They also helped the field turn its focus onto their key weakness—instability at temperatures relevant for processing, product fabrication, and even for use.

The reason that nanocrystalline metals are unstable is that grain boundaries typically are nonequilibrium defects, and have excess energies, which nature would prefer to eliminate through grain growth. The key to stabilizing nanostructures is therefore to either arrest the motion of the boundaries, or lower their excess energy to a point where the driving force for grain growth is effectively reduced below some practical limit, or both. Because both grain-boundary mobility and the local driving force for migration decrease with a reduction of the grain-boundary excess energy, [47,48] low-energy grain-boundary structures are generally preferable for stability. Several key strategies for stabilizing nanostructure thus focus on the structure of grain boundaries and methods to realize low-energy boundary configurations.

Two such strategies are the main focus of this article: the use of chemical additions (grain-boundary alloying) and the use of crystallography (low-energy grain-boundary configurations). In what follows, we review these two approaches, point to themes common to them both, and highlight interesting directions for future work.

Grain-boundary alloying: Intentional segregation

One of the concepts that has emerged as a critical one for stabilizing nanocrystalline structures is grain-boundary alloying. [49–57] By alloying a nanocrystalline metal with a second species that favors grain boundary segregation, it is possible to "decorate" the grain boundaries in the manner shown in **Figure 1**a through a Monte Carlo simulation of a hypothetical body-centered-cubic (bcc)

alloy, [58] and in Figure 1b through transmission electron microscopy chemical mapping in a Pt-Au alloy. [59] The chemical interaction of the alloying elements with the grain boundary can lower the excess energy of the grain boundary, and also provides a kinetic pinning contribution to stability of the structure. [60–63]

Virtually any alloying addition exhibiting a grain-boundary segregation tendency will attain some improvement in stability through this mechanism, so simply selecting known grain-boundary segregators is perhaps the simplest design approach for nanocrystalline alloys. A recent survey of studies of this kind [64] shows that when this approach has been used, it frequently improves stability up to typically around 300–500°C for dozens of alloyed nanocrystalline metals based on a number of base metals.

This level of stability provided a first critical step toward the application relevance of nanocrystalline metals. In particular, it permitted scaling and commercialization of coatings based on nanocrystalline alloys, because the synthesis of such coatings by, for example, electrodeposition, [65–75] involves processing temperatures well below the temperature where grains grow, so that the resulting product is nanocrystalline and stable for subsequent use up to several hundred degrees Celsius. **Figure 2** shows a series of contemporary coating products developed based on nanocrystalline Ni-W, [76,77] Al-Mn, [70,78] and Ag-W; [79–81] these commercial offerings are differentiated from competing coatings by their improved stability in the nanocrystalline state, gained through solute segregation at grain boundaries.

A more sophisticated approach to stable nanocrystalline alloy design, however, should consider more than just the grain-boundary segregation tendency alone. In recent years, researchers have gained an increased understanding of the structure and energetics of alloyed grain boundaries, and the energetic competition between decorated grain boundaries and competing phases such as solid solutions or ordered intermetallics. [50,82–85] In fact, it is phase competition that is the most important limiting factor in nanostructure stability in most alloys, because the energy of grain-boundary segregation is typically of similar magnitude to the formation energies of competing phases. This is illustrated in **Figure 3**, which is a survey of several hundred transition-metal binary alloys comparing the energy of solutes occupying grain boundaries (*y*-axis, more positive values being more favorable for segregation) with their energy in the most competitive second phase alternative (*x*-axis, more positive values being more favorable for second-phase formation). [84] The fact that the data exhibit some degree of positive correlation

reflect that in general, the energetic competition between grain-boundary segregation and second phases is rather close. Indeed, a survey in Reference 64 shows that the vast majority of nanocrystalline alloys that exhibit grain-boundary segregation lose their stability when the temperature is high enough to permit the formation of competing second phases, which deplete the grain boundaries of solute and trigger the onset of rapid grain growth.

The most successful cases of high-temperature stability in nanocrystalline alloys typically occur in alloys from the upper-left-hand corner of Figure 3, above the dashed blue line where the energy of grain-boundary segregation offsets both the intrinsic grain-boundary energy as well as the energy of second-phase formation. Some such cases have been achieved explicitly by design, using an analysis such as that of Figure 3. A few notable examples include those where high absolute temperatures up to 1200°C have been reported in refractory metals [50] and high homologous temperatures even above 0.75 T_m (with T_m the melting point) in other transition metals. [86–91]

In some cases where the energetics of grain-boundary segregation and second phases are very close at high temperatures, it is possible to attain an equilibrium in which both grain-boundary segregation and second phases are both present. Such a two-phase nanostructured equilibrium (a "nanoduplex" structure) was explicitly observed in the W-Cr system, [92] depicted in **Figure 4**a. Here, Monte Carlo simulations show how both grain-boundary segregation (in a nanocrystalline structure) as well as second-phase Cr precipitates are expected to coexist around 950°C, an expectation confirmed by transmission electron microscopy and quantitative microanalysis. Nanoduplex structures are especially technologically interesting, because both grain-boundary segregation and second-phase particles can contribute to stabilization, [93–95] and what is more, the second phase can impart additional properties not possible with a single-phase nanocrystalline structure, such as enhanced creep resistance [95] or improved processability. [96]

The equilibrium between a bulk phase and a grain-boundary segregation state previously described in connection with Figure 4a speaks to an important emerging concept in grain-boundary science with particular relevance to nanostructured materials. Namely, the configurations of grain boundaries are known to exhibit phase-like behavior, and so grain-boundary "phases" are sometimes explicitly described. [97–101] Some researchers use the term "complexion" to differentiate grain-boundary "phase" structures from bulk ones. [91,102–108] Whatever the nomenclature, the structure of a grain-boundary can undergo any number of transitions that are

phase-change-like, including segregated to desegregated, chemically ordered to chemically disordered, or crystalline to amorphous.

In segregation-stabilized nanostructures, complexion transitions involving desegregation are obviously relevant because they present a limit on stability. [92] In one case, in the NiTi-W system, an experimental demonstration has been provided for the spontaneous onset of grain-boundary segregation at high temperatures at a point where the bulk second phase began to dissolve, liberating solute to be available to segregate to grain boundaries. [109] Such behavior is opposite of classical expectations for grain-boundary segregation, where a segregation isotherm would expect less segregation at higher temperatures. Even more counterintuitive is the report that finer grains are favored at higher temperatures in the Fe-Au system, where the solid-state ferrite-austenite phase transformation is coupled to a segregation-desegregation transition at the grain boundaries. [110] Such remarkable effects are caused by the unique competition between phases and complexions that can occur in the "closed system" of a nanocrystalline structure with a high-volume fraction of grain-boundary sites.

The complexion concept also ties in closely with the notion of the grain-boundary "relaxation state." Grain boundaries, being structurally complex (and even more complex when alloyed), are configurationally close to many other related grain-boundary structures [111,112] with similar energy scales. Depending on the thermal history of the boundary, any number of structures may be accessed, with different energetics and implications for stability. The "relaxation state" of the grain boundary is thus adjustable, as commonly seen in works where nonequilibrium processing has led to "extra" disorder (free volume, dislocations, chemical mixity) in the boundaries, and a thermal anneal can lead to relaxation of the boundaries. [113–116] Such relaxation effects have a profound influence on mechanical properties and mechanisms. [117]

In many cases such relaxations at the grain boundary may be permanent, and it is not yet clear which activated states can be obtained simply by heating a grain boundary and relying on kinetically accessible structural changes. Greater understanding of the role of entropy [118] and the full spectrum of grain-boundary segregation states [119] will almost certainly be needed to address such issues. However, to the extent that grain-boundary structural changes are related to a complexion transition, they may also be reversible and even tunable. This enticing prospect has been documented, for example, when grain boundaries have been amorphized at high temperatures

in nanocrystalline Cu-Zr [91,107] or Ni-W [120], and subsequently quenched in to achieve dramatic effects on the resulting material properties.

Promoting low-energy grain-boundary crystallographies

Beyond using chemistry to manipulate the boundary energy, developing methods to evoke crystallographically "special" grain boundaries with intrinsically low excess energies is also a prominent strategy to enhance stability of nanocrystalline metals. There is a large and growing body of work focusing on nanostructures with an abundance of low-energy boundaries such as twin boundary and low-angle boundaries.

Owing to the extremely low excess enthalpy of twin boundaries, the thermal stability of nanotwinned structures in metals is generally superior to those of nanograined structures. [121] For example, nanoscale twins in a 330 stainless steel remain unchanged after annealing at 0.5 T_m [122], while in a 316 stainless steel with nanotwinned grains embedded in nanograins, annealing at 750°C led to the loss of the nanograined structure through recrystallization into microsized grains, yet the nanotwinned grains of the same composition survived. [123,124] In a magnetron-sputtered nanotwinned Cu film, no significant thickening of twin lamellae was detected after annealing at 0.8 T_m. [125] Nanolaminates with low-angle grain boundaries in pure Ni exhibit an onset temperature for thickening at 506°C, higher than the coarsening temperature of nanograins of comparable sizes (443°C). [126]

Beyond twin structures, even general high-angle grain boundaries exhibit a wide range of different atomic structures, and there are often nearby boundary configurations that can be accessed with lower energy and mobility. "Relaxing" general grain boundaries into lower energy states can be achieved through various mechanisms. Conventional thermally activated relaxation mechanisms include the annealing out of excess boundary dislocations, rearranging atoms in the grain-boundary region to effect a more uniform free volume distribution, [48,127] the formation of facets on specific low-energy planes, or the generation of local structural units with lower energies separated by junctions. [48]

Dissociation of grain boundaries through interaction with partial dislocations provides an alternative mechanism for their relaxation. Molecular dynamics simulations on a range of symmetric tilt boundaries in several metals showed that as partial dislocations are emitted, the original grain boundary may dissociate into two or even three boundaries connected by stacking

faults, leading to atomic relaxation in the surrounding region and decreasing the excess defect energy. [128] This model of grain-boundary relaxation was verified by high-resolution transmission electron microscope observations in Au and Cu. [129] It is also supported by measurements of atomic transport kinetics: the interaction of grain boundaries with a high density of twin boundaries was associated with an obvious structure relaxation of the boundary itself in Cu. [130]

In many ways, the observation that partial dislocations can relax grain boundaries is expected based on the extensive investigations over the past decades on plastic deformation mechanisms in nanocrystalline materials. Molecular dynamics simulations showed that the governing deformation mechanism of some face-centered-cubic (fcc) metals may shift from full to partial dislocation activities when the grain size is smaller than the dislocation splitting distance, which depends upon the resolved shear stress and stacking fault energies. [131,132] A similar critical grain size was proposed in terms of the classical dislocation theory, below which the critical shear stress for nucleating a full dislocation exceeds that for a partial. [133] According to the Frank–Read-type source model, the critical size for the full-to-partial dislocation transition in plastic deformation was estimated to be about 70 nm in Cu. [134,135] In fact, a number of experimental observations verified that partial dislocations become a major strain carrier for very fine nanograins (e.g., below 10 nm for Ni-Mo alloys. [116]) Given the high excess energy of the grain-boundary network, it is reasonable to expect that equilibrium would favor deformation mechanisms that constructively interact with (i.e., decrease) that excess energy. Some simulations have even directly connected mechanical work with grain-boundary relaxation. [136]

The possible mechanical relaxation of grain boundaries through their interaction with partial dislocations has been established experimentally on several pure fcc metals. By using a surface mechanical grinding treatment, a surface layer of gradient nanograined structure was produced on a coarse-grained Cu: [137] grain sizes are about 40 nm in the topmost surface, increasing gradually to 200 nm at 150 μm depth. With this structure, grain-size effects on the plastic deformation mechanism and grain-boundary relaxation can be examined within a single specimen. Microstructure observations showed that deformation is governed by full dislocations for grains larger than 70 nm and by partial dislocations in smaller grains, in which high density through grain twins and stacking faults are detected. Calorimetric measurements showed that the excess grain-boundary energy is around 0.40–0.55 J/m^2 for grains of about 100 nm, but drops to

0.28 and 0.21 J/m^2 for grains with sizes of 65 and 40 nm, respectively. These values are only about half of the conventional GB energy [137] (**Figure 5**). This remarkable drop in apparent grain-boundary energy coincides with the grain sizes at which partial dislocations begin to dominate plasticity, and suggests that such mechanisms better relax grain boundaries than do conventional mechanisms of plasticity. Relaxed boundary structures were identified under high-resolution transmission electron microscopy [137] that are analogous to the extended grain boundary structure with emission of partial dislocations [129] previously described.

This transition in grain-boundary energy is also closely correlated to a change in thermal stability: [134] whereas grains initially above about 70 nm in size quickly coarsened and recrystallized into much coarser (microcrystalline) grains at temperatures above 100°C, the finer grains with lower grain-boundary energies remained nanocrystalline up to ~350°C. **Figure 6** shows a cross-sectional comparison after annealing at 150°C for 1 h, with the topmost surface layer remaining stably nanocrystalline. **Figure 7**a summarizes the grain growth in these samples; the apparent grain coarsening temperature is about 250°C for 50-nm grains, which is much higher than that for larger grains (about 100°C for 80 nm and 140 nm). Interestingly, the coarsening behavior across this range of grain sizes is not monotonic; grains with sizes of about 70 nm exhibit the lowest thermal stability with grain growth setting on at only 0.28 T_m.

For metals with low stacking fault energies such as Cu, annealing twins often appear accompanying recrystallization of deformed structures. This provides an alternative approach to triggering grain-boundary relaxation, [138] namely, by inducing thermal twinning before grain growth upon heating. One way to achieve this is by rapid heating to postpone the nanograin coarsening process, [139] since heating rate hardly affects the formation temperature for annealing twins [140–142]. As an experimental demonstration of this concept, gradient nanograined Cu samples were heated at a rate of 160 K/min to 250°C, generating copious annealing twins in those nanograins with sizes ranging from 60 to 140 nm; high-resolution micrographs are available in Reference 138. As shown in Figure 7b, the coarsening temperatures of these grains after such treatment increased by hundreds of degrees to ~500°C.

Finally, it is important to note that while this article has primarily reviewed stability with respect to thermal exposure, mechanical deformation can also lead to coarsening in nanocrystalline materials. [143–145] Generally, thermal stability seems to correlate with mechanical stability of the grain structure in such cases, and for the present example of nanocrystalline Cu relaxed through

rapid annealing this is demonstrably true. [146] After quasistatic tensile deformation of the gradient nanograined Cu specimen to a strain of 0.3, the fractional grain-size change ($\Delta D/D_0$) showed an obvious peak as a function of initial grain size, as shown in **Figure 8**. The peak of this trend lies at ~75 nm, very close to the critical grain size for thermal stability, implying that grain-boundary relaxation has a similar effect on the mechanical stability of nanograins. This observation is supported by more detailed structural characterizations, and has also been confirmed in other materials including Ni and Ag. [146] Similarly, mechanical stability also increased remarkably in specimens subjected to rapid annealing treatment rather than mechanical relaxation. As also shown in Figure 8, 80-nm grains after such relaxation treatment show $\Delta D/D_0$ values below 10% for the same conditions. [146]

Conclusions and future outlook

The coarsening tendency in nanocrystalline metals is extremely strong, and practical engineering materials with nanoscale structures need to be specifically designed for stability. While there are many strategies to slow and stop grain growth in materials science, in nanocrystalline materials the amount of interfacial area is so large as to both demand and enable new approaches. This article summarized efforts to lower the grain-boundary energy of nanocrystalline metals, through two complementary approaches:

- **Grain-boundary alloying** uses the chemical binding energy between added solutes and grain boundaries to lower the excess boundary energy and bring nanocrystalline structures closer to equilibrium. While any system that exhibits grain-boundary segregation can, in principle, show improved stability, this article highlights the critical role of phase competition with grain-boundary segregation as a critical feature in nanocrystalline systems. With a high volume fraction of grain boundaries, the complexion or phase-like behavior of the boundaries themselves has substantial influence on the overall system energy and stability. Better understanding of multiphase and multicomplexion structures is needed, and preliminary progress in this area is already leading to interesting new materials and processing paths for next-generation nanocrystalline alloys. More work is needed to understand specific grain-boundary structures, and the competition for solute amongst many such structures in a complex nanocrystalline environment.

- **Low-energy crystallographic structures** are energetically favored, but kinematically not always easy to access in polycrystalline structures. Here, the role of twins and stacking faults as special low-energy configurations has been highlighted. Not only can twins and other special boundaries help resist coarsening in nanostructures, but partial dislocations and stacking faults can facilitate the local reordering and relaxation of more general high-angle grain boundaries. When either deformation or rapid annealing treatments are used to effect such relaxations, a nanocrystalline structure can be dramatically stabilized, both against thermal coarsening and deformation-induced structural change. The interaction between these types of treatment is an area needing further exploration, and the extension of these methods to other materials and form factors would be highly desirable. The ease of such treatments certainly speaks to significant future technological opportunities.

Both of these approaches share a goal of lowering grain-boundary energy, and in both cases, it is clear that the local atomic details of the boundary structure are critical to the global stability of the resulting material. These details are reflective of the "relaxation state" of the boundaries, and are difficult to quantify and generally lacking comprehensive understanding. The effect of these "relaxed" boundaries on stability of the global grain-boundary network in the nanostructures needs clarification in future studies. Greater understanding of such subtle structural effects, and their accessibility through thermal and mechanical processes, will certainly be a major focus of future work in this field, and should lead to significant advances in the development of future stable nanocrystalline metals.

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Conflict of interest statement

MIT has filed patents based on the research of C.A.S. on this topic; Xtalic Corporation licenses some such patents and C.A.S. works with the company on some of their commercial alloys.

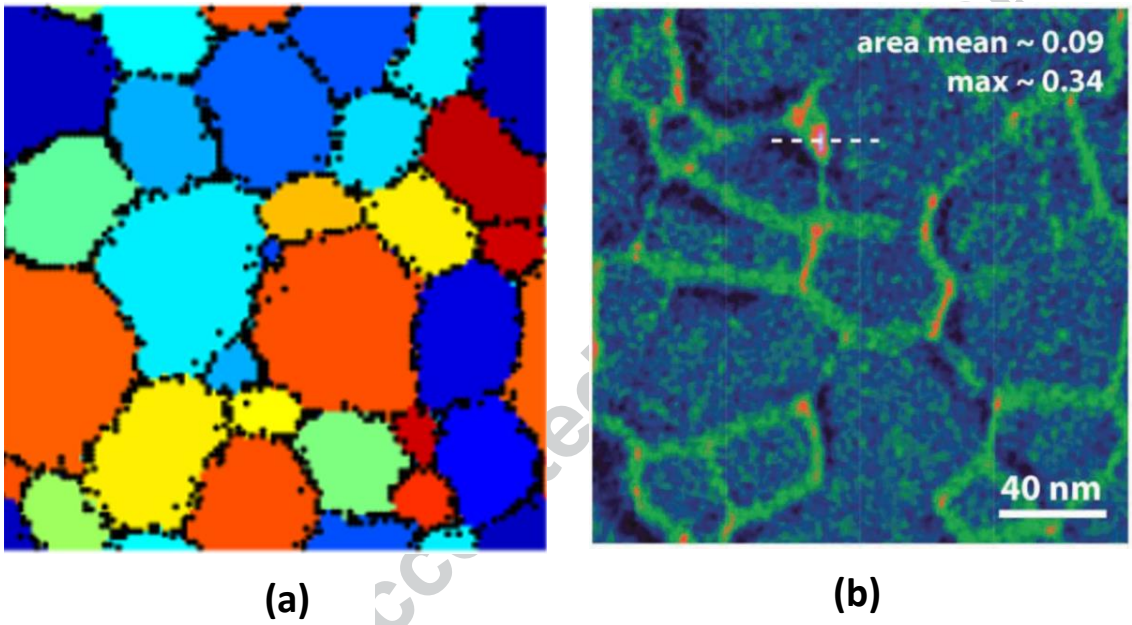

Figure 1. Nanocrystalline alloys can be stabilized by segregation of solutes to the boundaries, lowering the boundary energy and also providing kinetic impediments to grain-boundary migration. This is illustrated by equilibrium Monte Carlo simulations for a body-centered-cubic (bcc) alloy structure,[58] and by scanning transmission electron microscopy and chemical mapping by energy dispersive spectroscopy of a Au-Pt alloy.[59] The simulated structure in (a) is for a generic bcc material and has no formal length scale, although the edge length spans 100 atoms, which for bcc tungsten amounts to ~30 nm.

Figure 2. Grain-boundary segregation contributes substantial stability to electrodeposited nanocrystalline alloys, permitting their wide usage for protective coatings where the high strength, wear resistance, and other functional properties of the nanocrystalline state are of interest. (a) An enterprise electronic connector architecture with a 35-mm short dimension on the plug face. The connector metal set features W-stabilized nanocrystalline Ni alloy coating layers. Courtesy of Amphenol Inc. (b) Components of an electric vehicle connector for very high-power applications, comprising a nanocrystalline Ag-W and Ni-W coating stack for operation above 200°C. The pin on the left is 50 mm in length. Courtesy of Xtalic Corporation. (c) 75-mm long bolts coated with a stabilized nanocrystalline Al-Mn alloy coating for aerospace applications. Courtesy of Xtalic Corporation.

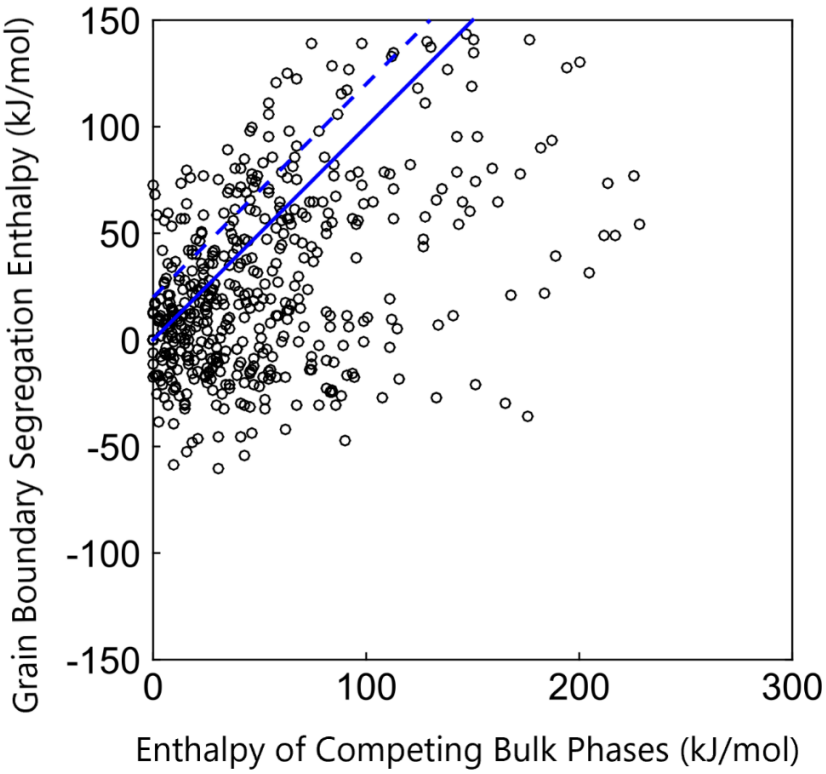

Figure 3. A survey of several hundred binary transition-metal alloys, comparing the enthalpy of grain-boundary segregation (*y*-axis) with that of the nearest competing bulk phase, including solid solutions and ordered compounds (*x*-axis). All of the points lying above the line of equality (solid blue line) represent alloys in which the grain-boundary segregated state is energetically preferred. For points further above the dashed blue line, segregation can also offset the full energy of the grain boundary itself, leading to stable nanocrystalline alloys with decorated boundaries as in Figure 1. Reprinted with permission from Reference 84. © 2017 Elsevier.

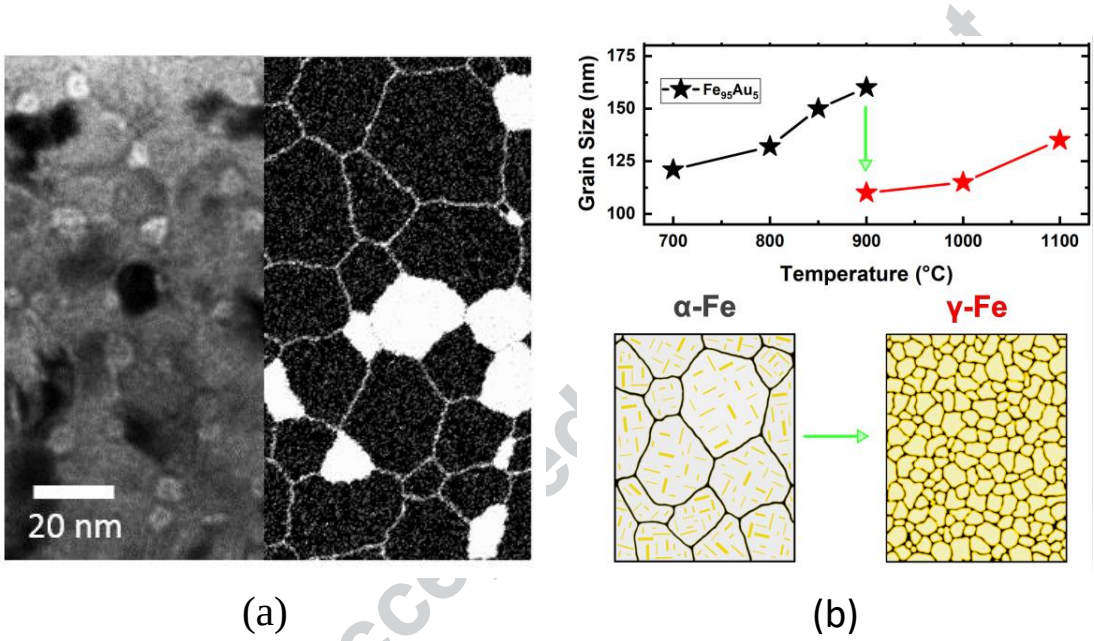

Figure 4. Examples of alloys in which bulk phases and grain-boundary segregation are both energetically preferable conditions, leading to complex equilibria unique to nanostructured systems. (a) A "nanoduplex" structure in the W-Cr system, where both second-phase Cr particles and grain-boundary segregation of Cr on W nanograins are present together at 950°C, illustrated through both transmission electron microscopy and lattice Monte Carlo simulations (on the same scale).[147](b) I*n situ* x-ray measurements of grain size in the Fe-Au system, where the allotropic phase transformation leads to dissolution of Au and shrinkage of the grains to a smaller nanoscale size; the schematic illustrates the putative evolution, involving greater grain-boundary segregation (and thus smaller grains) in the high temperature phase. Reprinted with permission from Reference 110. © 2018 American Physical Society.

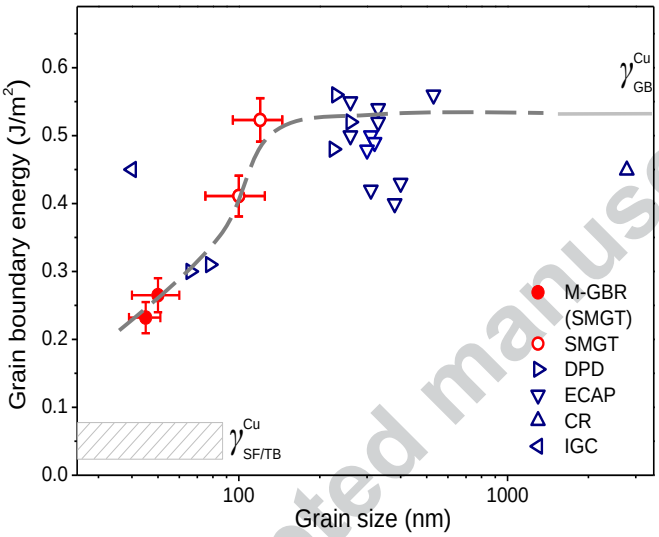

Figure 5. Measured grain-boundary energy as a function of average grain size in Cu. Literature data for Cu processed with different techniques are included. Note: DPD, dynamic plastic deformation; [148] ECAP, equal-channel angular pressing; [149,150] CR, cold rolling; [151] IGC, inert gas condensation. [152]) Conventional values for the polycrystalline grain-boundary energy (γ_{GB}) and energy for stacking faults and twin boundaries ($\gamma_{SF/TB}$) in Cu are also indicated.[137]

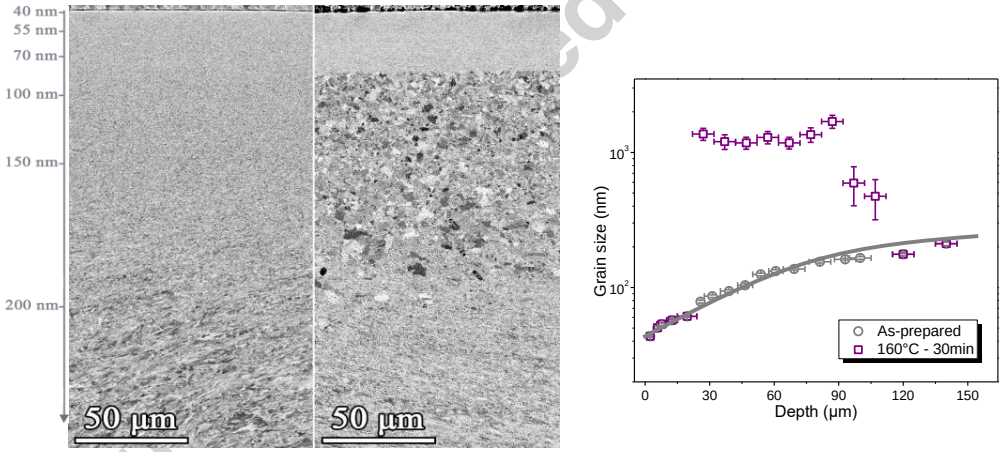

Figure 6. Typical cross-sectional scanning electron micrographs of an as-prepared gradient nanograined Cu sample (left) and that after annealing at 160°C for 60 min (right). The average grain sizes along the depth in the as-prepared sample are displayed. The average grain-size distributions along the depth in the as-prepared sample and the annealed sample are plotted (right). Reprinted with permission from Reference 138. © 2020 AAAS.

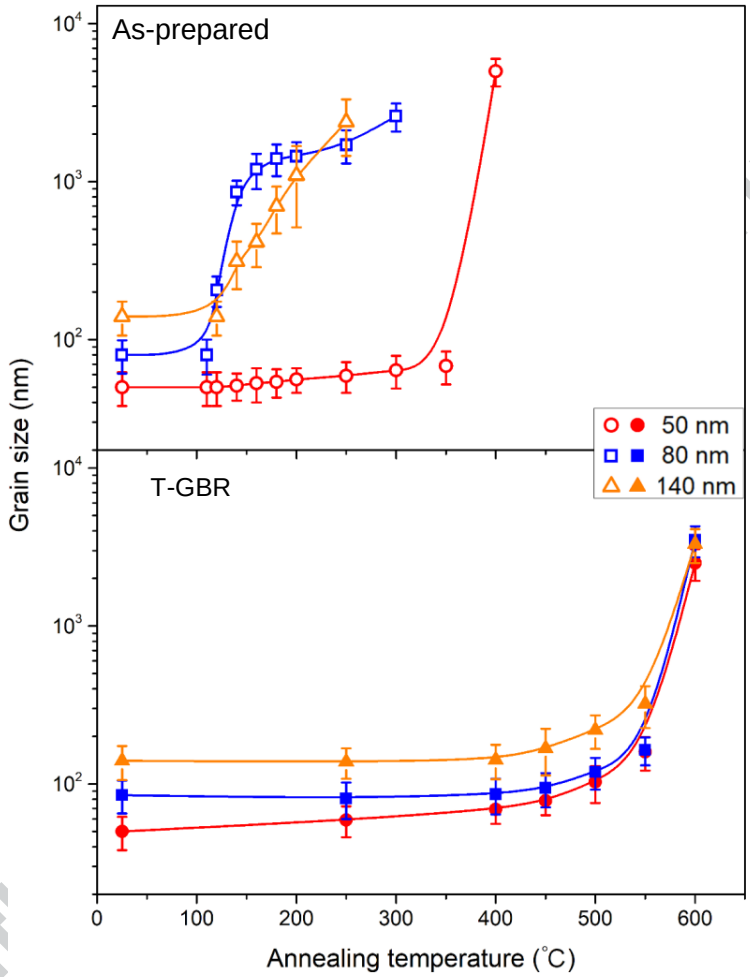

Figure 7. Variations of grain sizes with the annealing temperature for three samples with the average grain sizes of 50, 80, and 140 nm, respectively. Hollow symbols represent the as-prepared samples and solid ones represent the thermally relaxed (T-GBR) samples after rapid-heating (160 K/min to 250°C). Error bars are standard errors of the average grain sizes. Reprinted with permission from Reference 138. © 2020 AAAS.

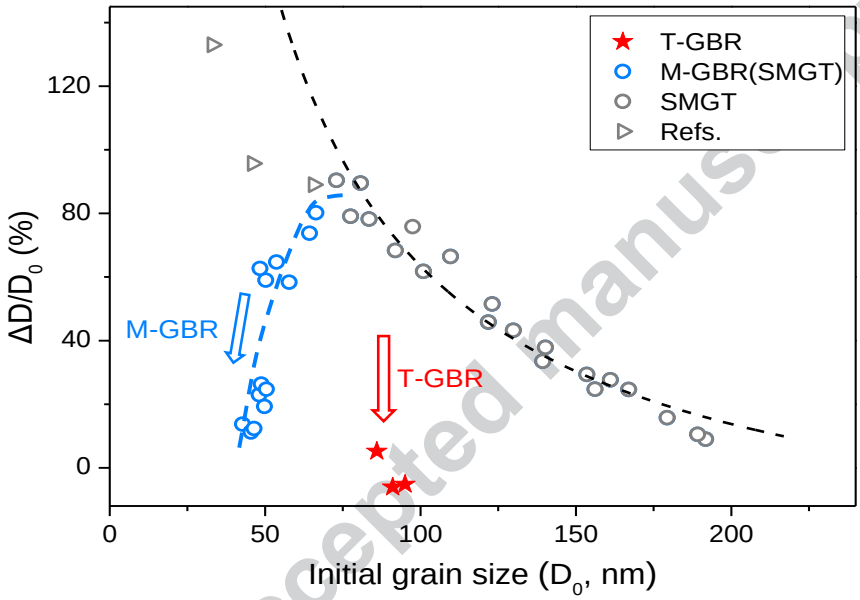

Figure 8. Variations of the measured relative grain-size change ($\Delta D/D_0$) as a function of initial grain size (D_0) for Cu after tension with a strain of 0.31 for samples subjected to mechanical grain-boundary relaxation (M-GBR by surface mechanical grinding treatment, SMGT) and thermal grain-boundary relaxation (T-GBR [i.e., after rapidly annealing the SMGT sample at 250°C]). Data from T-GBR samples after tension with a strain of 0.3 are presented as stars. Data from the literature [153–155] are included for comparison.[146]

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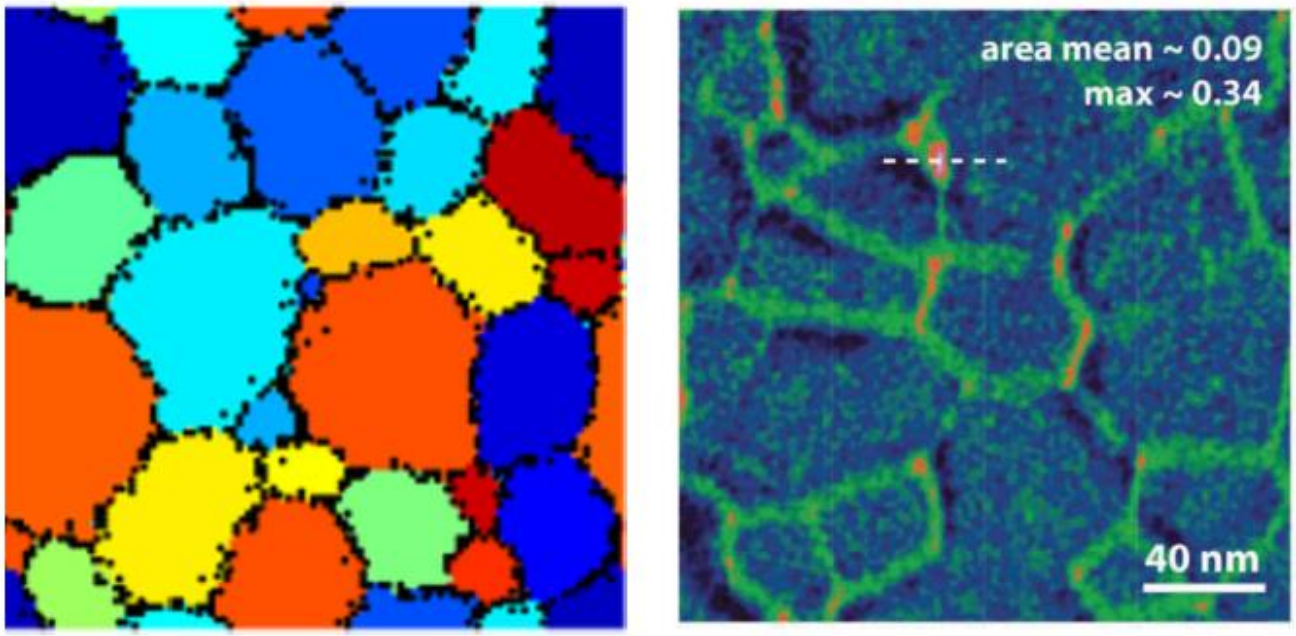

(a) (b)