

# The role of complexions in metallic nano-grain stability and deformation



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## ABSTRACT

Nanocrystalline metals have excellent strength due to the high density of grain boundaries inside. However, these same boundaries lead to limited thermal stability and a tendency to fail in a brittle manner, issues which limit the practical usage of these materials. Most strategies for stabilization of nano-grains against coarsening rely on the idea of using segregating dopants to lower excess boundary energy. The theory of interface complexions is a useful tool for describing the thermodynamics behind segregation as well as identifying distinct segregation patterns. Some of these same complexions can also dramatically alter mechanical behavior. Unlike past strategies, which always result in a trade-off between strength and ductility, the addition of complexions can potentially increase ductility while retaining or even increasing strength. In this paper, we discuss how complexions offer a unique opportunity to address these limitations simultaneously. In addition to reviewing the current-state-of-the-art, important areas where innovation is needed are also identified.

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## 1. Introduction and motivation

Nanocrystalline metals are defined as having an average grain size ( $d$ ) less than 100 nm. This dramatic grain refinement brings an equally dramatic increase in the volume fraction of material that is located at the grain boundaries, with the geometric analysis of Palumbo et al. [1] showing that roughly 30% of the material is located in the grain boundaries for an average grain size of 10 nm. With this rising grain boundary volume fraction comes a large increase in strength, often greater than an order of magnitude higher than the strength of microcrystalline metals. For example, coarse-grained Cu only exhibits a yield strength of ~50 MPa [2], while the yield strengths of nanocrystalline Cu samples with grain sizes of  $d = 26$  nm and  $d = 30$  nm were reported to be 535 MPa [3] and 760 MPa [4], respectively. This extreme strengthening has been observed for many metallic systems, often opening new avenues for the use of a particular material. For example, Al is an extremely light metal but tends to be weak in its pure form. Elemental Al is not widely used as a structural metal, with heavy alloying required to increase strength to an acceptable level even for use in aerospace applications, where limiting weight is the major priority. On the other hand, pure Al can be strengthened to levels comparable to steel alloys by grain refinement to the

nanometer range [5]. Other advantages of nanostructuring include increased resistance to wear [6,7] and fatigue [8]. However, the two major limitations of nanocrystalline materials can also be connected to the preponderance of grain boundaries: (1) *limited thermal stability* and (2) *lack of ductility*.

Grain boundaries, like all defects, have an excess free energy associated with the deviation from the preferred crystalline arrangement of atoms. Nanocrystalline metals therefore have a very large driving force for coarsening of the grain structure, in order to reduce the interfacial area inside the material. As a result, pure or elemental nanocrystalline metals are typically unstable and rapidly coarsen [9,10], with significant grain growth sometimes occurring even at room temperature [11]. Loss of the nanostructure means that the targeted high strength will be lost as well, making the stabilization of nano-grains at service temperatures a key goal in this field. In addition, this lack of thermal stability has an important implication for the practical production of nanocrystalline metals. Processing routes for bulk nanostructured materials can be loosely broken into “top down” techniques, where a coarse-grained microstructure is refined (usually by severe plastic deformation), and “bottom up” techniques, where small quantities of material are assembled to create a bulk material. Unfortunately, although it is relatively simple to create bulk materials with top down techniques, these methods are often limited to refinement into the so-called ultrafine grain regime, with grains less than 1000 nm but larger than 100 nm. Alternatively, bottom

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up techniques, such as ball milling powder samples, can reduce grain size to  $\sim 20$  nm in many cases, but require a consolidation step for the fabrication of bulk pieces. Since consolidation requires the application of a high temperature, typically  $>50\%$  of the melting temperature, increased thermal stability is also required to enable the scalable production of nanocrystalline metals [12].

Nanocrystalline metals have extremely high strength, but this is almost always accompanied by a dramatic decrease in ductility. For example, nanocrystalline Cu created by surface mechanical attrition only exhibits a total plastic strain-to-failure of 3% [4], an extremely low value for a metal. A general trend is observed where strength and ductility of nanocrystalline metals are mutually exclusive properties [13]. One can either have a strong yet seemingly brittle response, or a soft and ductile behavior. For example, Gianola et al. [14] demonstrated that mechanically-induced grain boundary migration can give nanocrystalline thin films additional ductility when this mechanism is activated, but these samples are much weaker than expected. Fracture surfaces from nanocrystalline materials show evidence of dimpled rupture [15], a signature that the nano-grains themselves are able to sustain plasticity. However, this intrinsic ductility of each nano-grain does not translate to macroscopic or extrinsic ductility. Appreciable ductility is required of most structural materials, so that catastrophic failure is avoided. Although yield is typically defined as a failure, it is preferred that a component deforms irreversibly yet survives and can still carry load, as opposed to shattering or crumbling soon after yield. A ductile response is also helpful for processing tasks, where shaping into a final form often requires plastic flow.

In this article, we discuss the current state-of-the-art strategies used to address the limited thermal stability and ductility of nanocrystalline metals, with an eye toward exploring how the theory of complexions can be useful for understanding important behavior and enabling further developments. We first provide a brief overview of some of the important aspects of complexion theory that are especially relevant to this discussion. We then focus on the two challenges of thermal stability and mechanical behavior one at a time, isolating the important physical phenomena behind each limitation and identifying opportunities for innovation in both areas. As these behaviors are intimately related to grain boundaries, direct control over interfacial structure, chemistry, and properties should have a dramatic impact. The unique opportunity offered by complexion engineering is not just that it can address these issues, but rather that one material design methodology may be able to simultaneously address both.

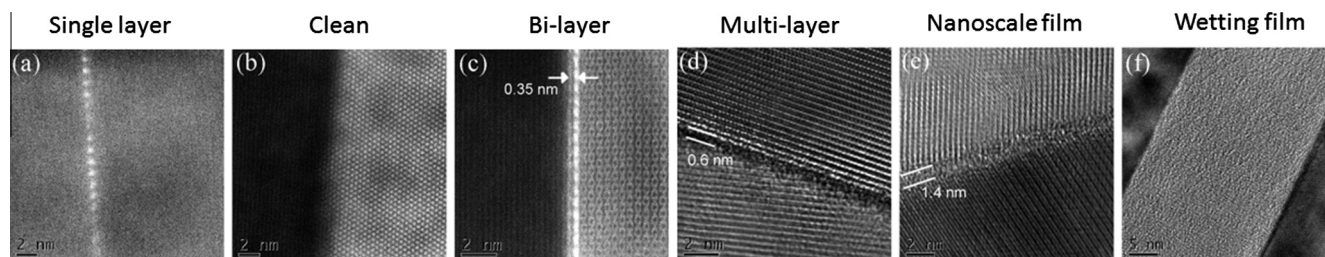
## 2. Complexions: Distinct interfacial states

Materials scientists have long acknowledged that grain boundaries can be thought of as two dimensional “phases-like” features which can undergo structural transitions at critical values of

temperature or chemical composition [16–18]. The term **complexion**, denoting interfacial material that is in thermodynamic equilibrium and has a stable finite thickness, has recently been adopted in the literature [19–21]. Complexions do not technically adhere to the strict definition of a phase introduced by J.W. Gibbs since their structure depends on the orientation and chemistry of the neighboring crystallites [22]. The concept of distinct and thermodynamically-stable interfacial structures can be traced back as far as 1860 when surface premelting was proposed by Faraday [23]. Unfortunately, excitement for such an idea waned over time, as it became clear that complexions were exceedingly rare and difficult to access in single element systems. For example, Hsieh and Balluffi [24] performed in situ transmission electron microscopy (TEM) heating experiments and found that grain boundaries in pure Al do not premelt even at temperatures as high as  $0.999 T_{\text{melting}}$ . However, recent efforts have shown that these interfacial complexions become much more common and accessible in multicomponent systems [25–28].

Dillon, Harmer, and coauthors recently created a categorization scheme that relies on complexion thickness based on high-angle annular dark field scanning TEM observations in doped  $\text{Al}_2\text{O}_3$  [19]. Six discrete Dillon-Harmer complexions were found, as shown in Fig. 1, with each displaying a different grain boundary mobility as measured by grain growth kinetics. These include: (I) a single layer of dopants, (II) clean grain boundaries, (III) bi-layers, (IV) multi-layers, (V) nanoscale films of equilibrium thickness, and (VI) wetting films. All of the structures shown, with the exception of the wetting film which is actually a bulk phase sandwiched between two new complexions (the interfaces between the original crystals and the new film), have a thickness which is determined by thermodynamics. While reports of complexions are much more common in materials with directional bonding such as ceramics [29], analogous examples of similar complexions have recently been reported in metallic systems [20,30,31].

The Dillon-Harmer complexion types are only one of many possible categorization schemes. A number of other options exist, with characteristics like complexion geometry, composition, and even changes to misorientation or boundary normal used a differentiating features. However, any scheme includes simplifications of some kind that cannot capture all possible degree of freedom, meaning multiple variations are often necessary for a complete description. For a discussion of nano-grain stability and mechanics, we will rely heavily on the Dillon-Harmer classifications but it is also important to consider the periodicity found within different complexions. Complexions can either have a recognizable degree of periodicity (ordered) or a lack of long-range order (disordered) in either structural units or chemical composition. For example, complexion Types I–IV above would be structurally ordered, as atoms are arranged in a set number of layers. On the other hand, Types V and VI can be either structurally ordered, with a crystalline film forming, or disordered, with an amorphous/glassy structure to the film. Chemical order is less closely tied to the six



**Fig. 1.** High-angle annular dark field scanning TEM images show the variety of complexion types that can be observed in doped  $\text{Al}_2\text{O}_3$ . These include (a) single layer segregation, (b) clean grain boundaries, (c) bi-layer segregation, (d) multi-layer segregation, (e) nanoscale films with equilibrium thickness, and (f) wetting films. Different degrees of structural and chemical disorder can be found with this variety of complexions.

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