# Spatial variation of short-range order in amorphous intergranular complexions

Zhiliang Pan [a], Timothy J. Rupert [a,b,*]

[a] Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA 92697, USA
[b] Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697, USA

## ABSTRACT

Amorphous materials lack long-range order but short-range order can still persist through the recurrence of similar local packing motifs. While the short-range order in bulk amorphous phases has been well studied and identified as an intrinsic factor determining the material properties, these features have not been studied in disordered intergranular complexions. In this work, the short-range order in two types of amorphous complexions is studied with a Voronoi tessellation method. Amorphous complexions can have three distinct regions: amorphous-crystalline interfaces, regions deep inside the films that have short-range order identical to a bulk amorphous phase, and transition regions that connect the first two regions. However, thin amorphous films contain only the amorphous-crystalline interface and the transition region, providing further evidence of the constraints imposed by the abutting crystals. The thickness of the transition region depends on film thickness at low temperatures but becomes thickness-independent at high temperatures. Similarly, the complexion short-range order is dependent on the interfacing crystal plane at low temperatures, but this effect is lost at high temperatures. Our findings show that amorphous complexions contain spatial gradients in short-range order, meaning they are both structurally and chemically different from bulk metallic glasses.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Complexions are interfacial states that exhibit phase-like behavior under different thermodynamic conditions [1]. One way of categorizing complexions is by their thickness or levels of adsorbate, where six types have been identified by Dillon et al. [2]: (I) a single layer of dopants, (II) clean grain boundaries, (III) bilayers, (IV) multilayers, (V) intergranular films of nanoscale equilibrium thickness, and (VI) wetting films. While complexions I–IV are often structurally ordered with legible layers of dopants, complexions V and VI are often disordered [3], in which case they can be broadly grouped as amorphous intergranular films. Complexion V is an amorphous region sandwiched between two amorphous-crystalline interfaces separated by a distance of a few nanometers, with the thickness determined by interfacial thermodynamics, and is thus called a nanoscale intergranular film. Complexion VI is in fact a bulk amorphous phase sandwiched between two amorphous-crystalline interfaces. Amorphous intergranular films can lead to activated sintering [4–6] in ceramics and refractory

metals [7,8] and abnormal grain growth in other materials [2,9–11]. They can also assist grain boundary sliding [12,13] and suppress crack formation induced by grain boundary-dislocation interactions at grain boundaries [14,15], making it possible to fabricate tougher nanocrystalline materials [16]. Since amorphous complexions are important features for material fabrication, design, and optimization, the detailed atomic structure from which the physical and mechanical properties originate [17] are of great interest.

While long-range order determines the deformation mechanism of crystalline materials, short-range order from the repetition of local packing motifs controls the plastic deformation of metallic glasses [18]. It has been observed that full-icosahedral clusters, a common five-fold symmetric, quasi-crystalline packing motif in metallic glass, can increase strength but deteriorate ductility [19,20]. Shear banding, one of the possible plastic deformation mode common in bulk metallic glasses, has been connected to the breakdown of full icosahedral clusters from the microscopic perspective [21] and a decrease in the fraction of perfect icosahedral clusters is observed during the plastic deformation [22]. The short-range order in a bulk amorphous phase can be affected by fabrication parameters as well. For example, decreasing cooling rate can increase the fraction of icosahedral clusters [23]. Short-

range order can also be affected by ion irradiation which breaks stiff icosahedral packing motifs, leading to a softening effect within the cascade region [24]. In addition, short-range order has been connected with the thermal stability [25] and magnetic properties of metallic glasses [26]. Short-range order is also a theoretical foundation of an efficient cluster packing model [27], which has successfully predicted or estimated the density [28], glass forming ability, and thermal stability [29,30] of metallic glasses. Since short-range order plays such an important role in determining the properties of bulk amorphous phases, the local structural order of amorphous complexions is also of interest.

Experimental observations [31,32] have shown the repeated distribution of the same type of packing clusters in nanoscale intergranular films at the vicinity of abutting crystals, indicating the existence of short-range order at the amorphous-crystalline interfaces. However, these studies concentrated only on the structural order at amorphous-crystalline interfaces. Whether the short-range order exists and what type of structural order dominates the disordered interior was not investigated due to the limited resolution of experimental techniques. Nanoscale intergranular films and wetting films are both described as being structurally disordered, but are two different types of structures and have different alloy compositions, with the solute composition in wetting films higher than that in nanoscale films [3]. While the short-range order in bulk amorphous phase has been shown to be affected by alloy compositions [3], whether and how the difference in alloy composition in the two types of complexions leads to different structural order remains unknown. The alloy composition also changes with thickness for nanoscale intergranular films [3], suggesting that the short-range order might change with the film thickness as well. The short-range order observed in amorphous complexions is believed to be imposed by abutting crystals, decaying into the film interior with a distance from the amorphous-crystalline interface [33–35]. The test of this hypothesis makes it highly necessary to check spatial variation of structural order along the film thickness direction. Finally, the role of abutting crystals also implies that the structural order imposed by different crystals planes should be different. While atomistic simulations have the advantage of precisely describing atomic level microstructures over experimental observations and thermodynamic models, the vast majority of studies to date [34–39] have concentrated on film structure in ceramic systems. Much less work (see, e.g., [17]) has been performed for complexions in metallic systems.

In this work, the short-range order of nanoscale and wetting amorphous intergranular films in Cu-Zr binary alloys is analyzed with a Voronoi tessellation method [40,41]. This analysis method can provide detailed information about local clustering and has been successfully used in prior studies to describe bulk amorphous phases. Three distinct regions of structural order are identified, with the amorphous-crystalline interface, a transition region, and in the region deep within thick wetting films all having unique short-range order signatures. The transition region depends on overall film thickness at low temperature, but this effect goes away at high temperature. However, the structural order in amorphous-crystalline interfaces is always independent of complexion type and overall film thickness. Complexion short-range order is also shown to depend on the interfacing crystal plane at low temperature, but again this effect does not exist at high temperatures. This finding suggests that the constraint of the abutting crystals is reduced as temperature increases.

## 2. Methods

Complexion formation was simulated with hybrid atomistic Monte Carlo/molecular dynamics simulations in Cu-Zr binary alloys at 600 K and 1200 K using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [42], with 1 fs integration time step used for all molecular dynamics simulations. Embedded-atom method potentials were used to describe the Cu-Cu and Zr-Zr interactions, while a Finnis-Sinclair potential was used to describe the Cu-Zr interactions [43]. The simulations started from a Cu bicrystal which was first equilibrated using a Nose-Hoover thermos/barostat at zero pressure and then doped with Zr solutes. The doping process was simulated with a Monte Carlo method in a variance-constrained semigrand canonical ensemble [44] while structural evolution and relaxation was simulated with molecular dynamics, with additional simulation details provided in Ref. [3]. This hybrid simulation technique can model dopant segregation and complexion transitions at different grain boundaries under a variety of thermodynamic conditions. Adaptive common neighbor analysis [45] was used to identify the local crystal structure of each atom, with face-centered cubic atoms colored green, hexagonal close packed atoms red, body-centered cubic atoms purple, icosahedral atoms yellow, and other atoms white. Zr atoms were highlighted as dopants with blue[1] color. Fig. 1(a) shows a bicrystal Cu sample containing two $\Sigma 5$ $(3\,1\,0)$ boundaries. Samples containing $\Sigma 11$ $(1\,1\,3)$, twist $(1\,0\,0)$ $36.86°$, twist $(1\,0\,0)$ $10.39°$, and twist $(1\,1\,1)$ $30°$ boundaries were also studied since connecting with different crystal planes of the abutting grains is expected to affect short-range order [33]. To facilitate a comparison, bulk amorphous phases were also produced through the hybrid simulation technique in a periodic simulation box having dimensions of $\sim 8 \times 8 \times 8$ nm. The Zr composition is fixed to 25.8 at. % at 600 K and 11.5 at.% at 1200 K, which are the Zr compositions of wetting films obtained at the two temperatures.

The samples were quenched with a conjugate gradient energy minimization technique to remove thermal noise yet preserve the grain boundary structure. A Voronoi tessellation method was then used to analyze the Voronoi polyhedron associated with each atom, which is enclosed by all of the bisecting planes of the lines connecting the center atom and its neighboring atoms. The Cu/Zr atomic size ratio is set to be 0.804 [27] to weight the bisection. Voronoi polyhedra can be described using the index notation $\langle n_3, n_4, n_5, n_6, \ldots \rangle$, where $n_i$ denotes the number of Voronoi polyhedron faces with $i$ edges and the sum of $n_i$ is the coordination number of the centered atom, since each face is associated with a neighbor of the center atom. The short-range order of a material then can be defined as the recurrence of the same type of polyhedron. The minimum edge length on the polyhedron is set to be 0.6 Å to make sure that the polyhedra associated with atoms in the grain interior are identified as $\langle 0, 12, 0, 0 \rangle$, a building block for perfect face-centered cubic crystals. To isolate the amorphous intergranular films, face-centered cubic atoms with $\langle 0, 12, 0, 0 \rangle$ polyhedron are excluded when calculating radial distribution functions and performing statistical analysis of the complexion structure.

## 3. Results and discussion

With increasing Zr content, the grain boundaries either transform gradually into nanoscale films and then wetting films, as shown in Fig. 1(b), which gives the grain boundary composition and grain boundary thickness as a function of global composition, as well as the typical equilibrium complexion structures found at these different stages. One way to show the structural order of a material is through its radial distribution function, which gives the number density of particles in a spherical shell centered at a reference particle. Fig. 2(a) shows such a function for the bulk