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Materials selection rules for amorphous complexion formation in binary metallic alloys

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ABSTRACT

Complexions are phase-like interfacial features that can influence a wide variety of properties, but the ability to predict which material systems can sustain these features remains limited. Amorphous complexions are of particular interest due to their ability to enhance diffusion and damage tolerance mechanisms, as a result of the excess free volume present in these structures. In this paper, we propose a set of materials selection rules aimed at predicting the formation of amorphous complexions, with an emphasis on (1) encouraging the segregation of dopants to the interfaces and (2) lowering the formation energy for a glassy structure. To validate these predictions, binary Cu-rich metallic alloys encompassing a range of thermodynamic parameter values were created using sputter deposition and subsequently heat treated to allow for segregation and transformation of the boundary structure. All of the alloys studied here experienced dopant segregation to the grain boundary, but exhibited different interfacial structures. Cu-Zr and Cu-Hf formed nanoscale amorphous intergranular complexions while Cu-Nb and Cu-Mo retained crystalline order at their grain boundaries, which can mainly be attributed to differences in the enthalpy of mixing. Finally, using our newly formed materials selection rules, we extend our scope to a Ni-based alloy to further validate our hypothesis, as well as make predictions for a wide variety of transition metal alloys.

1. Introduction

Internal interfaces can significantly influence material behaviors such as plastic deformation [1], fracture [2], and corrosion [3], and engineering these interfaces can in turn lead to improved performance [4,5]. An exciting new concept for the design and control of interfacial properties are “complexions,” interfacial structures that are in thermodynamic equilibrium and have a stable, finite thickness [5–7]. Complexions can be considered quasi-2D “phases” that only exist at an interface, surface, or grain boundary [8]. Similar to bulk phases, complexions can be described with thermodynamic parameters and can even undergo phase-like transitions in response to alterations of external variables such as temperature, pressure, chemistry, and grain boundary character [8]. Since their existence is dependent on the neighboring crystalline grains, complexions do not technically adhere to the Gibbs definition of a phase and thus are considered with a separate terminology [8,9].

Dillon et al. [6] developed a convention to classify complexions into six different types according to thickness, structural ordering, and composition. The six types suggested were: (I) sub-monolayer segregation, (II) clean, undoped grain boundaries, (III) bilayer segregation, (IV) multilayer segregation, (V) nanoscale intergranular films, and (VI) wetting films. This continuum of complexion types can be subdivided into ordered or disordered. Complexion types I-IV have crystalline structure and are classified as ordered, whereas types V and VI can assume either an ordered or disordered structure. The disordered versions of type V or VI complexions can be classified as amorphous intergranular films (AIFs) [6]. Different complexion types have been shown to dramatically influence material behavior and have been deemed the root cause behind several previously unexplained phenomena. Ordered bilayer complexions were found to explain liquid metal embrittlement in Cu-Bi [10] and Ni-Bi [11] due to the segregation of Bi to the grain boundaries which stretches the intergranular atomic bonds to near the breaking point, making them very fragile. Similarly, Ga segregates to the grain boundaries in Al-Ga to form an ordered trilayer

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complexion that also has an embrittling effect [12]. Conversely, AIFs have been shown in some situations to improve damage tolerance due to the excess free volume present in the amorphous grain boundary structure [13–15]. Atomistic simulations have shown that the amorphous-crystalline interfaces that bound AIFs can attract dislocations [15]. AIFs can also act as a toughening feature to delay intergranular crack formation and propagation [13,14], as well as increase radiation tolerance by acting as an efficient and unbiased sink for point defects [16]. Experimental studies support these findings, with nanocrystalline Cu-Zr containing AIFs demonstrating enhanced strength and ductility compared to the same alloy with ordered grain boundaries [17,18]. Amorphous complexions have also been shown to dramatically increase diffusion, which can cause abnormal grain growth [6] and solid-state activated sintering [19]. Solid-state activated sintering, referring to improved densification rates that occur below the solidus temperature, has been observed in both metallic and ceramic systems. The addition of a small amount of sintering aid element creates disordered intergranular films that act as a pathway for improved diffusion below the bulk eutectic temperature [13–16,19,20]. In addition, AIFs were recently found to stabilize nanocrystalline grain structures against grain growth at elevated temperatures, with a nanocrystalline Cu-Zr alloy remaining nanostructured even after a week at 98% of its melting temperature [18].

Due to the enhanced performance imparted by AIFs, the application of these unique grain boundary structures to a wider array of alloys would be advantageous. The hypothesis of surface premelting promoted interest in stable interfacial films [21], which lead to thermodynamic descriptions of 2D-interfacial films that undergo phase transformations [22–24]. Complexions have since been extensively studied in ceramics [6,8,25] and multicomponent metallic systems where AIFs are accessible [26,27]. Advancement of the thermodynamic theories behind complexions has even allowed for the development of grain boundary phase diagrams that connect structural transitions at an interface with alloy composition and temperature, emphasizing their phase-like behavior [7,19].

While the theoretical framework behind AIF formation is well-developed, the implementation of this concept to new alloy systems has been limited. The experimental study and application of these features has been largely relegated to ceramics where AIFs have been extensively observed [6,28], or in alloys where AIFs were already suspected, such as those alloys that exhibit the AIF-driven behavior of solid-state activated sintering [29]. Development of a general set of materials selection rules using readily available material parameters to predict material systems in which AIFs are possible would be powerful. The history of amorphous materials research can serve as an instructive example of this concept. In 1932, Zachariasen [30] offered a critical discussion of the structure of glassy ceramics and suggested general guidelines for materials selection, prompting a flurry of discoveries and advancements built upon these guidelines. Despite their rudimentary nature, Zachariasen's rules are recognized as one of the first attempts to systematically address glass forming ability, fundamentally influencing future research in the field [31]. Similarly, as interest began to build for amorphous metals, Inoue [32] suggested a set of three empirical rules that have since provided a preliminary guide for the development of new bulk metallic glasses (BMGs).

In this study, we propose materials selection rules for the promotion of AIFs that emphasize dopant segregation to grain boundaries and the creation of energetically favorable conditions for forming an amorphous region. To test the robustness of these rules, a variety of Cu-rich systems with contrasting thermodynamic parameters were selected and processed. Here, we focus on transition metal dopants in order to avoid complicating factors such as directional bonding, complex kinetics, and crystallographic anisotropy dependence that are characteristic of ceramic systems [19,33,34]. The behavioral patterns established by the inspection of the Cu-rich alloys are then extended to predict the complexion formation behavior of a new Ni-based alloy where AIFs have not yet been observed in prior work. In summary, the type of complexion formed at the grain boundaries of a polycrystalline binary metallic alloy can be controlled by an informed selection of enthalpy of segregation (ΔH^{seg}), enthalpy of mixing (ΔH^{mix}), and atomic radius mismatch, where AIF formation depends on dopant segregation to the grain boundary and the glass forming ability of the alloy.

2. Materials and methods

The alloys used in this study were produced with magnetron co-sputtering using an Ar plasma in an Ulvac JSP 8000 metal deposition sputter tool. Sputtering was specifically chosen in order to create high purity samples. High-purity targets were obtained from Kurt Lesker with purities of 99.99 wt.% for Cu, 99.2 wt.% (inc. Hf) for Zr, 99.9 wt.% (exc. Zr) for Hf, 99.95 wt.% (exc. Ta) for Nb, 99.95 wt.% for Mo, and 99.99 wt.% for Ni. In addition, deposition was only performed after a 10^{-7} mTorr base chamber pressure was achieved to further minimize impurity incorporation into the films. The films were deposited at 400 °C using an Ar pressure of 1.5 mTorr with sample stage rotation during deposition in order to achieve a uniform film. The metals were co-deposited onto Cu or Ni substrates which had been polished to a mirror surface finish prior to deposition. Films were deposited onto sheets of the primary alloying element in order to eliminate unwanted chemical reactions between the thin film and substrate during subsequent thermal processing. A summary of the key deposition parameters, processing details, and film information are presented in Table 1.

Since the average thickness of a transmission electron microscope (TEM) sample must generally be <100 nm in order to achieve electron transparency [35], very small grains can overlap, introducing uncertainty to structural and chemical analysis [36]. In order to minimize this issue, high sputtering temperatures were chosen in order to increase atom mobility and maximize grain size at deposition, as well as suppress the growth of a void-filled film [37]. A micrometer-scale film thickness was also targeted since the

Table 1
The sputter deposition parameters including substrate, deposition temperature, power, base pressure and deposition rate. Also included is the resultant film thickness, dopant percentage and final grain size of each alloy after all thermal processing treatments were completed.

Alloy	Substrate	Dep. Temp. (°C)	Solute/Solvent Dep. Power (W)	Ar Base Pressure (mTorr)	Dep. Rate (Å/sec)	Avg. Film Thickness (μm)	Post Quench Comp. (at.%)	Avg. Grain Size (nm)	$0.92T_{solidus}$ (°C)
Cu-Zr	Cu	400	75/150	1.5	1.8	1.94	4.3	99 ± 29	900
Cu-Hf	Cu	400	75/150	1.5	1.7	2.04	6.2	47 ± 12	915
Cu-Nb	Cu	400	75/150	1.5	1.6	1.92	2.7	468 ± 185	1000
Cu-Mo	Cu	400	75/150	1.5	1.6	1.82	3.3	85 ± 26	1000
Ni-Zr	Ni	400	75/150	1.5	0.9	1.34	5.5	40 ± 12	1100