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Atomic-scale analysis of liquid-gallium embrittlement of aluminum grain boundaries

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Abstract

Material strengthening and embrittlement are controlled by intrinsic interactions between defects, such as grain boundaries (GBs), and impurity atoms that alter the observed deformation and failure mechanisms in metals. In this work, we explore the role of atomistic-scale energetics on liquid-metal embrittlement of aluminum (Al) due to gallium (Ga). Ab initio and molecular mechanics were employed to probe the formation/binding energies of vacancies and segregation energies of Ga for $\langle 100\rangle$, $\langle 110\rangle$ and $\langle 111\rangle$ symmetric tilt grain boundaries (STGBs) in Al. We found that the GB local arrangements and resulting structural units have a significant influence on the magnitude of the vacancy binding energies. For example, the mean vacancy binding energies for $\langle 100\rangle$, $\langle 110\rangle$ and $\langle 111\rangle$ STGBs in the 1st layer was found to be −0.63, −0.26 and −0.60 eV, respectively. However, some GBs exhibited vacancy binding energies closer to bulk values, indicating interfaces with zero sink strength, i.e. these GBs may not provide effective pathways for vacancy diffusion. The results from the present work showed that the GB structure and the associated free volume also play significant roles in Ga segregation and the subsequent embrittlement of Al. The Ga mean segregation energies for $\langle 100\rangle$, $\langle 110\rangle$ and $\langle 111\rangle$ STGBs in the 1st layer were found to be −0.21, −0.09 and −0.21 eV, respectively, suggesting a stronger correlation between the GB structural unit, its free volume and the segregation behavior. Furthermore, as the GB free volume increased, the difference in segregation energies between the 1st layer and the 0th layer increased. Thus, the GB character and free volume provide an important key to understanding the degree of anisotropy in various systems. The overall characteristic Ga absorption length scale was found to be about ∼10, 8 and 12 layers for $\langle 100\rangle$, $\langle 110\rangle$ and $\langle 111\rangle$ STGBs, respectively. In addition, a few GBs of different tilt axes with relatively high segregation energies (between 0 and −0.1 eV) at the boundary were also found. This finding provides a new atomistic perspective for the GB engineering of materials with smart GB networks to mitigate or control liquid-metal embrittlement and more general embrittlement phenomena in alloys.

Keywords: Liquid metal embrittlement; Atomistic simulation; Grain boundary; Segregation

1. Introduction

Liquid-metal embrittlement (LME) is a phenomenon experienced by many intrinsically ductile metals, including aluminum (Al), nickel (Ni) and copper (Cu). These metals exhibit a drastic loss of ductility in the presence of certain liquid-metals, such as gallium (Ga), bismuth (Bi) and mercury (Hg) [1–10]. Understanding the mechanisms behind LME has been of particular interest in both experimental [2,3,5,8,10–25] and simulation [7,9,26–33] research. Discrepancies between experimental observations and

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modeling results have led to various proposals for LME mechanisms. One of the most widely accepted LME mechanisms suggests that penetration of the liquid-metal into grain boundaries (GBs) modifies interfacial energy so as to promote intergranular failure [3,9,10,20,22–24,29,34,35]. Consequently, the reasons for such variation are likely to be associated with the specific type of liquid environment [10,18,29] tested, whereby some elements act to enhance cohesion in certain systems, while others promote decohesion [28,35]. However, recent nanoscale experimental studies suggest that one of the primary contributing factors to LME is the formation of intermetallic compounds at GBs [1] and bilayer interfacial phases (e.g. in Ni–Bi) [17]. The lack of a definitive understanding of the mechanistic origin of LME hinders our ability to satisfactorily address LME in important technologies, including in the nuclear-power generation sector, where liquid-metal coolants are in contact with metallic structural components, and in industrial sectors that employ liquid-based joining technologies (e.g. soldering and brazing) [4,9,10,16,19,32].

Al–Ga is often viewed as a model LME system. Al and Ga are from the same chemical group (IIIA), have similar electronegativities and are of comparable atomic size [36]. Hence, they are expected to have similar chemical properties [27]. Nonetheless, liquid Ga penetration along Al GBs is rapid and results in a substantial loss of cohesion [32]. The effectiveness of LME in this system is known to depend on grain size [37]. Several experimental techniques have been employed to reveal the atomic-scale mechanisms that give rise to LME in this system. High-resolution transmission electron microscopy (TEM) has provided important insights into LME in Al–Ga [22–24]. While Ga does penetrate most GBs in Al, leaving behind Ga layers that range from one to several monolayers [9,22–24,27], in situ TEM studies have shown that low-energy boundaries, such as high coincident site density (small Σ) boundaries, show little segregation [23]. The interplay of the variables that influence embrittlement complicates distinguishing which properties affect and do not affect LME. The difficulties with preparing and fully characterizing experimental samples (especially their GB bicrystallography) has made the prospect of accurate simulations appealing. Atomic-scale simulations offer advantages for the analysis of GB properties, albeit at very small length and time scales. Nonetheless, such simulations can help establish the relationship between embrittlement and material/GB properties.

Atomistic and quantum mechanics-based simulations are increasingly utilized in investigations of fundamental LME mechanisms. Stumpf and Feibelman [27] employed first-principles methods to study Al–Ga and showed that Ga lowers the surface energy of Al. This is important since it suggests that Ga may lower the cohesive energy of interfaces in Al. The attraction of Ga to substitutional sites in Al GBs was demonstrated by Thomson et al. [26] using ab initio calculations for $\Sigma5(310)$ symmetric tilt grain boundaries (STGBs). They concluded that local strain governs the substitution characteristics. These efforts and others have shown that density functional theory (DFT) is effective for characterizing the electronic origins of LME. However, the computational expense associated with such calculations has limited their application to special GBs with a small number of atoms per cell. Monte Carlo and molecular dynamics (MD) methods have also been widely used to characterize LME [2,5,9,16,23,25,38,39]. While such calculations commonly incorporate a much larger number of atoms, they have been limited by their use of empirical descriptions of atomic interactions. Such potentials are typically fit to ab initio data and relevant experiments. Most of the early atomistic work quantified the role of GB structure on Ga penetration both with and without external stresses, suggesting that in some bicrystal systems, Ga penetration did not occur without application of external stimuli [5,23]. These studies indicate that GB characteristics play a significant role in embrittlement [39], leading to considerable interest in correlating GB structure with macroscale embrittlement. For example, MD simulations suggest that the atomistic mechanisms of LME are sensitive to boundary structure [29]. In another example, Nam and Srolovitz [32] found that Ga penetration in Al was smaller along symmetric GBs compared with asymmetric GBs, and that special low-Σ GBs are, indeed, special. The sensitivity of LME to GB structure and the fact that most studies focused on special boundaries provides impetus to explore how variations in structure and properties among large sets of general GBs influence LME.

GBs are two-dimensional defects which are characterized by five macroscopic degrees of freedom [40–48]. Saylor et al. [40] analyzed the GB character distribution (GBCD) in commercially pure Al and suggested that boundaries with low-index planes occur with particularly high frequency in polycrystals. The GB structure–energy correlation in several face-centered cubic (fcc) metals was investigated by Wolf [49] who established a linear relationship between GB energy and volume expansion per unit area (GB free volume). The role of the GB plane in determining GB energy was investigated by Holm et al. [43], who performed extensive calculations of GB energies in Ni and Al. Rohrer [50] established that the coincidence lattice site density (Σ) plays only a minor role as a determinant of GB energy in several systems and that the energies of the crystal surfaces that meet at a GB is a better indication of GB energy. Tschopp and McDowell [51] showed that asymmetric tilt boundaries in Cu and Al often decompose into lower-energy, symmetric tilt orientations via faceting. Hasson et al. [52] experimentally measured GB energies for a wide range of $\langle100\rangle$ and $\langle110\rangle$ STGBs in Al and concluded that lower-energy boundaries show unique segregation, corrosion and diffusion behavior.

In this paper, we perform a systematic investigation of LME in the Al–Ga system using ab initio pseudopotential calculations and molecular statics (MS) simulations to clarify the relation between GB structure, Ga segregation and the GB cohesive energy has LME fracture implications.