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Research Highlight

In this issue of the *CMSN Newsletter*, we are pleased to feature a research highlight from a newly formed Cooperative Research Team (CRT), Dynamics and Cohesion of Materials Interfaces and Confined Phases Under Stress: "Atomistic Mechanism of Liquid Metal Embrittlement," by Ho-Seok Nam (Princeton University) and David J. Srolovitz (Yeshiva University).

Atomistic Mechanism of Liquid Metal Embrittlement

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Dynamics and Cohesion of Materials Interfaces and Confined Phases Under Stress CRT

Summary: For many systems in which a liquid metal is in contact with a polycrystalline solid, deep liquid grooves form where the grain boundary meets the solid-liquid interface. For example, liquid Ga quickly penetrates deep into grain boundaries in Al, leading to intergranular fracture under very small stresses. By performing a series of molecular dynamics simulations of liquid Ga in contact with an Al bicrystal, Ho-Seok Nam and David Srolovitz, of the DCMICPS collaborative research team, have recently identified a novel mechanism for liquid metal embrittlement and have developed a new model for it.

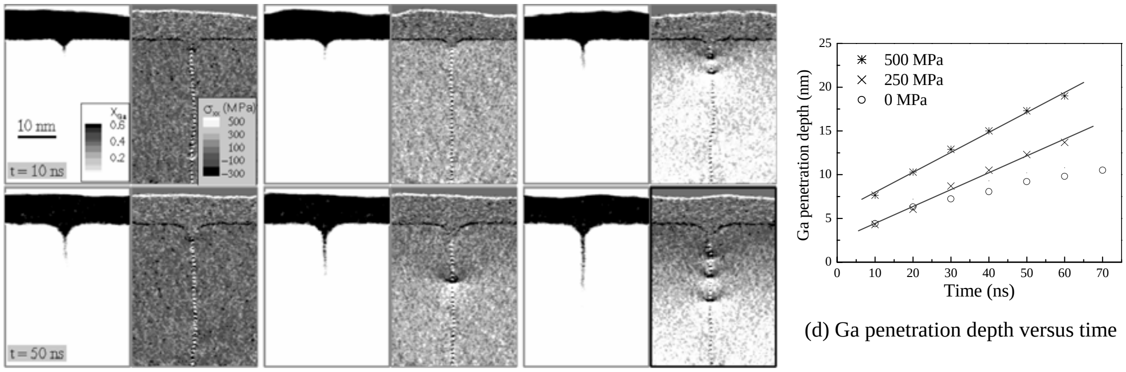
There are many examples in which very deep grooves form at the intersections of grain boundaries and the surface of systems where a liquid metal is in contact with a polycrystalline solid. In some systems, such as Al-Ga, Zn-Ga, Cu-Bi and Ni-Bi, the liquid film quickly penetrates deep into the solid along the grain boundary and leads to brittle intergranular fracture under the influence of even modest stresses. This is a form of liquid metal embrittlement (LME). Although this phenomenon is quite common in material processing, LME is not well understood. Liquid metal embrittlement is particularly important in nuclear reactor scenarios, where liquid metals are used as coolants and as spallation targets.

The Al-Ga couple is a particularly well-known LME system. Transmission electron microscopy (TEM) [1] and synchrotron radiation microradiography studies [2] show that liquid Ga penetrates into grain boundaries in Al at a remarkable rate, leading to distinct channel morphologies. The penetration of liquid Ga along the grain boundaries produces wetting layers with thickness ranging from several monolayers to several hundred nanometers, even in the absence of an applied load. Interestingly, the rate of propagation of such liquid layers is strongly influenced by very small stresses. These observations have led to the conclusion that liquid Ga embrittlement of Al is caused by rapid liquid Ga penetration.

Thermodynamically, wetting of a grain boundary by a liquid metal should be expected when the spreading coefficients S satisfies: $S = \gamma_{GB}-2\gamma_{SL} \geq 0$, where γ_{GB} and γ_{SL} are the free energies of the grain boundary and solid-liquid interface, respectively. However, thermodynamic arguments do not explain the liquid channel morphology, the Ga penetration kinetics, or the atomistic mechanism of Ga penetration. The anomalously fast, time-independent penetration rate (several μm/s at room temperature [1,2]) of very long nanometer-thick liquid films cannot be explained in terms of the classical Mullins grain-boundary grooving nor by normal grain-boundary diffusion.

Various models have been proposed to explain the kinetics and atomistic mechanisms by which the liquid phase penetrates quickly along grain boundaries [3]. While each of these approaches is capable of explaining one or more aspects of LME, each also leads to discrepancies with respect to other observed LME phenomena in the same materials system. For example, none of these approaches successfully explains the effects of stress on liquid film penetration. Nam and Srolovitz have studied LME by performing molecular dynamics (MD) simulations of an Al bicrystal in contact with liquid Ga (with and without an applied stress) and have investigated how Ga penetrates along the grain boundaries during the early stages of the wetting process. Based on the simulation results, a new mechanism for LME is proposed showing excellent agreement with both simulation and experimental data [4].

The atomistic mechanisms operating at the tip of the advancing Ga layers can be identified by analyzing the displacement and stress fields within the system. Figures 1 (a)-(c) show Ga concentration profile (left) and stress distribution (right) along a $\Sigma 5$ (301)/[010] symmetric tilt boundary at T=600 K at constant strains of 0, 0.65% (~250 MPa), and 1.3% (~500 MPa), respectively. Although the liquid groove shapes and wetting angle are nearly the same in Figs. 1(a)-(c), the Ga penetration is strongly enhanced by the application of stress, forming nanometer-thick Ga-rich films. The Ga penetration rate is estimated by noting the depth at which the Ga concentration along the grain boundary exceeds a fixed value (one monolayer) at each time. This depth L versus time t is plotted in Fig. 1(d). In the absence of an applied stress, the rate at which Ga penetrates down the grain boundary [slope in Fig. 1(d)] gradually decreases with time. However, when stress is applied, the Ga penetration rate becomes nearly time independent. Clearly, stress changes the fundamental nature of Ga penetration down grain boundaries in Al: the constant penetration rate suggests that Ga is not simply undergoing a random walk down the grain boundary ($L \propto t^{1/2}$) nor is the penetration rate controlled by normal grain-boundary grooving ($L \propto t^{1/3}$ or $L \propto t^{1/4}$) but, rather, is strongly driven ($L \propto t$). The Ga penetration rate increases with applied tensile stress and increasing grain size but is not affected by presaturating the liquid with Al. While stress promotes Ga penetration, it has little effect on the rate of Al dissolution into the liquid [4]. This implies that dissolution does not control liquid film formation in the Al-Ga system.



(d) Ga penetration depth versus time

(a) 0 MPa (b) 250 MPa (c) 500 MPa

Figure 1. Liquid metal penetration profiles at t=10 and 50 ns (from top to bottom) for simulations performed at T=600 K. The left panels of (a)-(c) show the Ga concentration profile (mole fraction X_{Ga}) and the right panels of (a)-(c) show the stress distribution (σ_{xx} in MPa) for simulations with an applied stress (a) of 0, (b) 250 MPa, and (c) 500 MPa, respectively.

The effect of stress on Ga penetration can be examined by considering the stresses within the system; σ_{xx} is shown to the right of the Ga penetration figures in Fig. 1. Figure 1(a) shows that in the absence of an applied strain, the stresses in the system are small and random. However, when a strain is applied, we observe the formation of one [Fig. 1(b)] or more [Fig. 1(c)] patterns of concentrated stress at the grain boundary. These patterns consist of a dark (large compressive) region above a light (large tensile) region. This suggests that these stress concentrations are associated with edge dislocations with a Burgers vector perpendicular to the boundary plane. Examination of the atomic structure of the grain boundary [Fig. 2(a)-(b)] shows the existence of an interfacial dislocation at the location of the center of this stress pattern. Following the approach of Hirth and Pond [5], we identify the Burgers vector to be **b**=(1/10)[301] [see Fig. 2(b)]. We confirm this measurement by analytically calculating the stress field associated with such dislocations [6] using the measured bicrystal elastic properties and comparing it with the stress field determined in the simulation, as shown in Fig. 2(c). The excellent correspondence confirms that the normal component of the Burgers vector is $b_n = |\mathbf{b}| = a_0/\sqrt{10} = 1.28$Å, where a_0 is the lattice parameter.

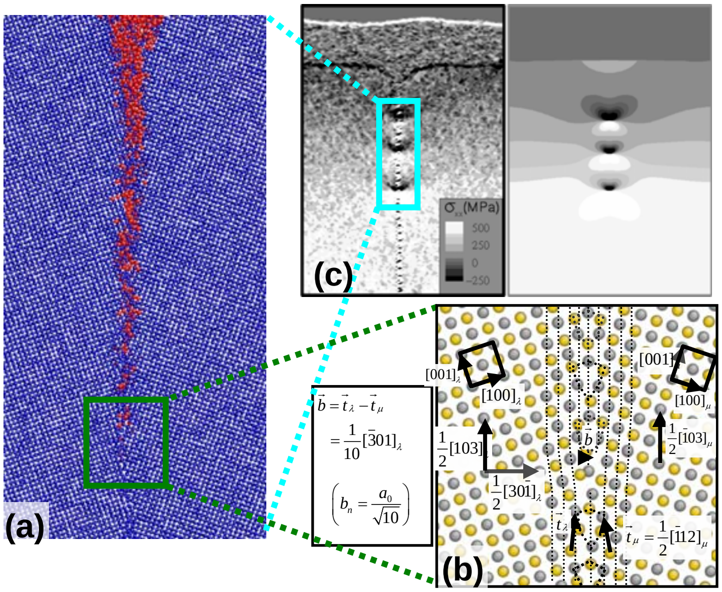


Figure 2. (a) Atomic scale image of Ga penetration along $\Sigma 5$ (301)/[010] symmetric tilt boundary in an Al bicrystal. The atoms shown in blue represent Al atoms and those in red are Ga.
(b) Enlarged view of dislocation core region (Burgers circuit). Atomic structure was quenched in order to remove thermal noise. The grey and yellow circles represents rows of atoms with positions in alternating (020) planes.
(c) Comparison of the MD simulation (left) and linear elastic stress field (right).

It is interesting to note that in the absence of an applied strain, no dislocation forms [Fig. 1(a)] and the Ga penetration rate decreases with time [Fig. 1(d)]. However, when a strain is applied, dislocations form and climb at a fixed rate [Fig. 1(b) and (c)] and the Ga penetration rate is time independent [Fig. 1(d)]. This suggests that the constant Ga penetration rate observed in the strained solid is associated with the fixed rate of "climb" of dislocations. A new picture of LME emerges. First, Ga diffuses down the grain boundary in Al below the liquid groove root and causes stresses large enough to nucleate a dislocation in the grain boundary. The first dislocation "climbs" down by stress-enhanced Ga hopping across the dislocation core, leaving a tail of Ga behind. This Ga hopping leads to a constant dislocation climb rate that is independent of applied stress. Once the dislocation moves far enough from the groove root, another dislocation is nucleated. It too climbs down the grain boundary at the same rate, resulting in a uniform spacing of climbing dislocations. With Ga at the grain boundary, applied strains enhance the grain-boundary opening and, in turn, more Ga is inserted from the liquid groove into the grain boundary to relieve the residual stress (i.e., Ga layer thickening process). The Ga penetration rate mirrors the dislocation climb rate and hence is time independent. In order for LME to occur, the solute must diffuse quickly in the grain boundary, a stress must be applied to nucleate dislocations and keep the grain boundary open, and the solute must be capable of creating grain-boundary decohesion at sufficient concentrations.

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CMSN Information

CMSN's teams, oversight, and administration are listed below. Further information can be found at http://www.phys.washington.edu/~cmsn.

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Dynamics and Cohesion of Materials Interfaces and Confined Phases Under Stress	Mark Asta (University of California at Davis), Alain Karma (Northeastern), and Anthony Rollett (Carnegie-Mellon)
Predictive Capability for Strongly Correlated Systems	Richard Scalettar and Warren Pickett (UC-Davis)
Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials	Dieter Wolf (INL) and Simon Phillpot (University of Florida)
Multiscale Studies of the Formation and Stability of Surface-based Nanostructures	Zhenyu Zhang (ORNL & University of Tennessee) and Kai-Ming Ho (Ames Laboratory and Iowa State University)
Fundamentals of Dirty Interfaces: From Atoms to Alloy Microstructures	Alain Karma (Northeastern University) and Anthony Rollett (Carnegie Mellon University)
Magnetic Materials Bridging Basic and Applied Science	Bruce Harmon (Ames) and Malcolm Stocks (ORNL)
Excited State Electronic Structure and Response Functions	John Rehr (Washington) and Steven Louie (UC-Berkeley)
Microstructural Effects on the Mechanics of Materials	Dieter Wolf (INL) and Richard Lesar (Sandia)

CMSN Oversight

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