Full length article

Highly choreographed atomic motion and mechanism of interface amorphization

Yiying Zhu [a], Guanglan Liao [a, **], Tielin Shi [a], Zirong Tang [a], Mo Li [b, *]

[a] *State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science & Technology, Wuhan 430074, China*
[b] *School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

A B S T R A C T

Atomic mechanisms are investigated for solid-state amorphization using a diffusion couple made of metallic glass $Cu_{46}Zr_{54}$ and single-crystal Al. Our extensive molecular dynamics simulation reveals that amorphization occurs in the crystalline metal at the interface via a series of highly coordinated and complex atomic motion involving all elements in both the glassy phase and the crystal. Chemical mixing occurs through asymmetric interdiffusion of more Cu and Zr in the glass phase into the crystal than Al into the glass. The faster diffuser Cu is found to hop into the Al lattice position, whereas Zr trails behind and provides a supporting role by pulling Al atoms off the lattice position. This highly choreographed atomic motion creates cooperative diffusion and mixing at the interface region that causes large lattice distortion and eventually leads to the collapse of the crystalline phase when critical amounts of Cu and Zr are fused into Al. Extension of this atomic mechanism to a more general setting is discussed, particularly in the context of elastic instability.

© 2016 Published by Elsevier Ltd on behalf of Acta Materialia Inc.

1. Introduction

Amorphization is omnipresent in many systems and occurs under a wide variety of conditions [1]. For example, when different crystalline phases, alloys or pure metals, are in contact or mixed, including Ni/Zr [2], Co/Zr [3], Si/Ge [4] bi- and multi-layers, or are irradiated with high-energy neutron or ions [5], the crystalline phases transform into a metastable amorphous or glassy phase. Perhaps the most simple example is the amorphization induced by a solid-state reaction in which a pure metal is put in contact with another or with hydrogen [6]. In all these cases, amorphization occurs in crystals with the characteristics of a first-order phase transition via nucleation and growth of the glassy phase in the interface region. In the solid-state reaction, the amorphous phase forms at the surface first and subsequently grows into the crystalline phase as hydrogen simultaneously diffuses. It is generally believed that amorphization occurs when the amorphizing reaction is faster than the alternative process of forming equilibrium crystalline phases, including compounds and crystalline solid solutions. In other words, the kinetic constraint is strong enough that

the more stable crystalline phases cannot form before amorphization occurs [7].

Although the thermodynamic and kinetic measurements support the foregoing explanation, the microscopic process still remains an open problem, particularly the corresponding atomic mechanisms. For instance, the intermixing of the metallic elements or hydrogen are driven by the negative heat of mixing between the elements, but how and where these diffusing atoms move, particularly inside the crystal lattice before, during and after amorphization transition, is unknown. Due to their small size, hydrogen atoms are likely to move through interstitial sites in metals. However, how do metallic elements that are too large to take advantage of interstitial positions move through a lattice? Furthermore, what are the causal and quantitative relations between intermixing or diffusion, and amorphization? In addition, when the reacting elements are mixed, how does the crystalline phase lose its stability and become amorphous? Is the cause a mechanical instability, as perceived in some atomistic models, or the formation of an amorphous phase nucleus before growth? [1] Furthermore, the transition takes place in relatively large gradients of chemical concentration or strain/stress field during mixing or reaction. Thus, how do chemical and property inhomogeneities affect the transition pathway and mechanism?

Amorphization generally occurs in interface regions between

* Corresponding author.
** Corresponding author.
   E-mail address: mo.li@mse.gatech.edu (M. Li).

heterophases, either different crystals, crystal-hydrogen interfaces, or crystal-amorphous interfaces. The small dimensions and transient nature of the amorphization transition at the interface limits experimental measurement. As a result, the questions posed above and others pertaining to the metastable phase transition remain open, despite their importance in completing our understanding of the crystal-to-glass transition. We expect that the answers will not only provide atomic-scale information supporting the thermodynamic and kinetic explanations [1] but also open up new approaches to the statistical physics formulation of metastable phase transitions.

In this work, we investigate the atomic mechanisms of amorphization at the interface of a diffusion couple made of metallic glass and pure metal. This type of sample undergoes a different amorphization process from that observed in pure metal-metal samples, for example, in multi-layer systems [1–4]. This choice of sample is based on the following considerations. Pure crystalline diffusion couples, or bi- and multi-layers, have been used widely in experiments [1–4,6,7] and atomistic simulations [8–10]. Amorphization is found to occur at the interface and proceed into both crystalline phases. By using a crystal phase in contact with an amorphous phase, we can reduce the complexity of analyzing the atomic mechanisms that would occur otherwise in both crystalline phases. Second, although much is known about amorphization in crystalline diffusion couples from thermodynamic and kinetic points of views [1], the atomic mechanisms of the amorphization process between amorphous and crystalline solids have not received much attention; only a few studies have been reported [11]. In fact, the amorphous-metal diffusion couple represents a large class of the heterogeneous materials widely used in scientific research and solid-state amorphization applications, including metal-metal samples. For example, in mechanical-deformation-induced amorphization processes, an amorphous phase forms at the crystal-crystal interface, whereas some metals remain crystalline and in contact with the amorphous phase [12]; even in metal-metal and metal-hydrogen diffusion couples, an amorphous layer forms soon after the reaction starts at the interface, and the subsequent amorphization proceeds in the remaining metals sandwiched between the amorphous phases and the metal or hydrogen [2–4]. Thus, our choice of the amorphous-metal diffusion couple establishes a specific perspective from which to understand amorphization in general.

Another reason for the choice is related to the recent developments of metallic glasses (MGs) with high strength and high toughness [13] by bonding MGs with various metals. Due to the disordered atomic structure, localized shear banding renders MGs with low plasticity and brittleness at room temperature, which largely limits their applications [14]. If bonded with other materials, such as a metal, the blocking layer introduced into an MG is expected to obstruct the shear banding such that the mechanical performance is improved and large parts with complex shapes can be manufactured, which is necessary in certain critical applications, such as those in the aerospace, nuclear energy and microelectronics industries [15]. Diffusion bonding is one method for joining MGs and metals. When the two materials are placed in contact, an amorphous diffusion zone appears and grows gradually, with interdiffusion between the elements [16]. The properties and performance of the joint depend critically on the amorphous zone.

Therefore, in this work, we investigate the amorphous-metal interface and amorphization using a $Cu_{46}Zr_{54}$ MG and single-crystal Al diffusion couple with a particular emphasis on the atomic mechanisms of *how the crystal phase becomes amorphized*. Molecular dynamics (MD) simulation is used to explore atomic-level information [17,18]. Our extensive simulation reveals that amorphization occurs in the crystalline Al at the interface by

nucleation and growth via a series of highly coordinated and complex atomic motions involving all elements in both the MG and pure metal. Cu and Zr are observed to diffuse asymmetrically from the glass phase into the crystalline Al during chemical mixing. The faster diffuser Cu is found to hop into the crystalline Al lattice position, whereas Zr trails behind and plays a supporting role by pulling Al atoms off the lattice. This highly coordinated atomic motion produces cooperative diffusion at the interface region that eventually leads to lattice distortion and collapse of the crystalline phase when critical amounts of Cu and Zr are fused into Al. To the best of our knowledge, this is the first detailed account of the atomic mechanism of amorphization.

2. Sample preparation and simulation method

We select $Cu_{46}Zr_{54}$ MG and single-crystal Al to create diffusion couples. The simple binary metallic glass, which exhibits good glass formability [19], represents a large class of good glass formers, as observed experimentally, that are usually complex, composed of multiple components and stable at room temperature. Therefore, the system we use is sufficiently simple to be modeled without losing generality. With the addition of a certain amount of Al, CuZr MG formation can be enhanced significantly [20], which suggests that Al should also be a good bonding material with the MG to form the desired layered composite structure.

To obtain atomic-level properties, we use the large-scale atomic/molecular massively parallel simulator (LAMMPS) [21]. The interactions between atoms are described with the embedded atom method potential [22,23], $E_i = F_\alpha(\sum_{j \neq i} \rho_\beta(r_{ij})) + \frac{1}{2} \sum_{j \neq i} \varphi_{\alpha\beta}(r_{ij})$, where F is the embedding energy, ϕ is a pair potential interaction, and α and β are the types of atoms i and j, respectively. To mimic experimental conditions, we use isothermal and isobaric, or NPT, ensemble MD with a time step of 1 fs, and the sample is placed under periodic boundary conditions in all directions.

We first melt the CuZr alloy at 2100 K and then quench it to 300 K at a rate of 2 K/ps to obtain glass. After relaxation to reach equilibrium at 300 K for 20 ps, the billet is made into a diffusion couple with Al. As depicted in Fig. 1a, the MD diffusion couple is a sandwich heterostructure consisting of two crystalline Al blocks with dimensions of 121 Å × 121 Å × 80 Å and a $Cu_{46}Zr_{54}$ MG block in the middle with dimensions of 121 Å × 121 Å × 100 Å. Three typical crystallographic orientations along the (100), (110) and (111) planes are selected for Al in contact with the MG. To avoid introducing large initial stress at the interface when we place Al and MG together, we first select the lateral dimensions for Al parallel to the interface and then cut the MG to fit this size because the latter has no fixed periodicity in atomic arrangement and thus can be "cut" as close as possible to the size of the Al block. The coordinate system is shown in Fig. 1 for the (100) Al-MG diffusion couple, with the z-direction along the diffusion couple and the x- and y-directions in the (100) plane. The same setup is chosen for the diffusion couples oriented along the (111) and (110) planes.

The model diffusion couple is relaxed at 300 K for 2 ps to reach thermal and mechanical equilibrium and then heated to 700 K at a rate of 20 K/ps. This process is used to bring the system to an elevated temperature and thus allow diffusion to be observed within the short time accessible to the MD simulation. The temperature of 700 K is below both the melting temperature of Al (T_m=933 K) and the glass transition temperature of the $Cu_{46}Zr_{54}$ MG (T_g=839 K); thus, the diffusion couple is kept in the solid state. The equilibrated configuration at 700 K is shown in Fig. 1b. We then reset the clock and start counting the time required for diffusion and amorphization for 6000 ps (Fig. 1c–e).

We should mention that the diffusion couple made in this