

Nanometer Scale Dynamics in Diffusion Limited Propagation of Interfaces in Amorphous Alloys

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(Received 22 September 1998; revised manuscript received 17 May 1999)

We quantify the nanometer scale avalanche dynamics of a propagating interface using time-resolved electron microscopy of binary amorphous Ge-Al alloys, which were heated and crystallized in a transmission electron microscope. Our observation of Ge-Al combines spatial resolution of nanometers with a time resolution of 0.04 sec. We find that the interface propagates by avalanches with a characteristic size of 10^5 atoms. We develop a model that represents the amorphous phase as a random mixture and treats the diffusion process in the crystalline phase; we find that the model results agree with experiment.

PACS numbers: 81.10.Fq, 61.43.-j, 64.70.Kb

The growth of a crystalline phase in the liquid or amorphous phase is a long-standing research subject. From an academic point of view, it reflects the most common version of a phase transition [1]. From a technological point of view, applications of crystal growth vary from mechanical to electronic products. The dynamics of the interface is of particular interest and has received special attention in recent years. Experimental studies on the interface dynamics are so far limited to optical microscopy with low resolution [2]. However, recently new experimental methods of electron microscopy make it possible to obtain the kinetics of the interface at the nanometer scale with a resolution of <0.1 sec [3]. Koster, using a conventional electron microscope, studied intensively the crystallization of amorphous alloys [4]. Here, we report on the dynamics of amorphous binary alloy crystallization at the nanometer scale.

The geometrical and dynamical aspects of interfaces propagating in random media have recently been intensively studied theoretically and experimentally [5]. Often, the interfaces reveal self-similar or self-affine geometry and their dynamics are characterized by sudden changes in local velocity resulting in the avalanche-type of interface propagation. In many cases, the geometry of the interface is not pure self-similar or self-affine but can be characterized by one or several length scales. The same is true for the avalanches sizes and duration. The existing theoretical models of surface growth [5] apply to a very limited set of experiments. Theoretical understanding of interface dynamics in various real experimental situations remains problematic.

Our study includes both experiment and theory on the diffusion-limited propagation of crystalline phase in an amorphous binary alloy. We have already reported various aspects related to the crystallization of amorphous Ge:Al thin films [6–8]. The details of the preparation of the films were described elsewhere [6]. Briefly, thin films, 200 Å thick and of Al-Ge alloys containing about 50% of each element, were prepared by simultaneous evaporation

of Al and Ge from two electron guns. The substrate is a microscope slide covered by soluble material that enables the separation of the film from the substrate.

The films were examined in a transmission electron microscope (TEM), Philips EM300, and the amorphous ones were selected for crystallization studies. These films were heated to a temperature of 250 ± 5 °C in the TEM during observation, using a commercial heating holder. At a temperature above 230 °C, crystallization occurs. The crystalline phase consists of colonies, each of them composed of a large Al crystal that contains subgrain boundaries. In these Al crystals, Ge precipitates to create a core with multitwinned structure and branched morphology. The average velocity of the crystalline front is as slow as a few angstroms per second. Such slow velocities enable video recording (by a large angle camera, Gatan model 673) at a variety of magnifications. This procedure enables one to study the dynamics of the crystallization process. Moreover, the process can be stopped at any time, simply by stopping the film heating. Such a procedure is extremely useful for studying the interface by various methods of microscopy and analysis such as conventional transmission electron microscopy (CTEM), electron diffraction, high resolution transmission electron microscopy (HRTEM), microprobe and nanoprobe chemical analysis. It was found that [6] (i) the growth velocity has the same activation energy as the diffusion of Ge in Al divided by the Al rim width. (ii) No concentration gradient was found in the amorphous phase near the interface. (iii) The Al-amorphous interface is rough down to an atomic scale with amorphous nanopockets in the Al crystalline phase. (iv) Both interfaces are coupled with a fixed (averaged, in time and space) distance between them for each crystallization temperature.

From these experimental studies, combined with theory [7,8] and computer simulations [7], we concluded that two processes are involved in the crystallization of the alloy: (1) diffusionless growth of Al in the amorphous phase, and (2) diffusion-controlled growth of the Ge core inside

the Al crystal. The crystallization rate is limited by the diffusion of Ge atoms through this Al rim.

We study the propagation of the interface between the crystalline Al and the amorphous phase. This interface is shown in Fig. 1a. Contour lines corresponding to the Al/amorphous interface at given moments were produced by computer analysis using a Synoptics image analysis system equipped with a "SEMPER 6+" program. A sequence of such lines at intervals of two video frames (0.08 sec) is shown in Fig. 1b. The propagation of the interface

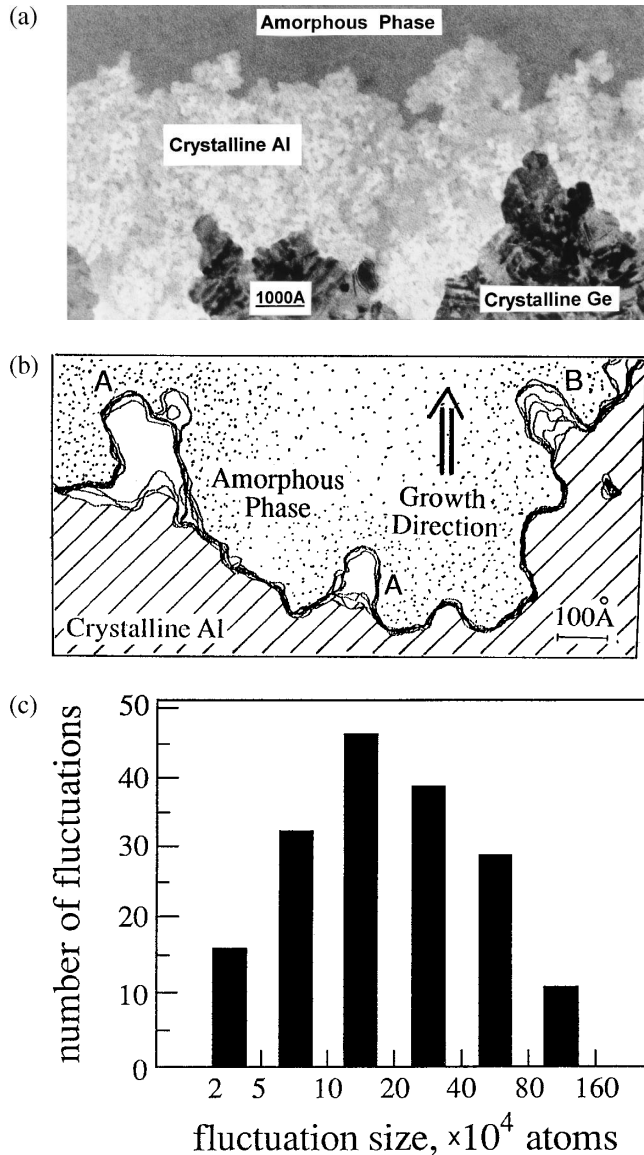


FIG. 1. Results of experiments. (a) An electron micrograph of the crystalline-amorphous interface. The Ge branches are partially seen. (b) Time-resolved characterization of the interface; a sequence of interface lines with intervals of 0.08 sec (every other video frame). Note that this panel is magnified roughly 10 \times compared to part (a). (c) The distribution of avalanche sizes obtained from quantitative measurements of about 200 avalanches.

is made up of two components: continuous growth and local fluctuations. Although thermal drift and the signal-to-noise ratio prevent conclusive results about the continuous growth, we nevertheless can clearly detect local fluctuations in the velocity (for which the resolution is limited only by the standard video resolution of 0.04 sec).

Based on the video records analysis analogous to that of Fig. 1b, we study the following characteristics of the fluctuations.

(1) The local direction of propagation has no "one-to-one" correlation with the general direction.

(2) The average speed of the interface is a few angstroms per second; however, (a) at any moment within the video frame resolution (0.04 sec), only a few percent of the interface length is actively propagating by an avalanching mode. (b) Some of the avalanches (B) grow continuously at a speed of 200 Å/sec. Other avalanches (A) are faster, >1000 Å/sec. The video limitation of the time resolution prevents our finding the exact value.

(3) The existence of a characteristic length scale for the avalanche was evaluated by direct measurement of the avalanche size. The direct measurements correspond to the projected area of the avalanches. Considering isotropy in three dimensions, the distribution of a characteristic avalanche size of 1.5×10^5 atoms is found (see Fig. 1c). This characteristic size is equivalent to a sphere approximately 100 Å in diameter (the distance between atoms is ≈ 2 Å).

A branched morphology—which indicates that diffusion is controlling the crystallization process—is found in various alloys. We believe that modeling the process in the Ge:Al amorphous alloy is applicable to other quenched systems. It is probably also valid for liquid-solid transitions, although the redistribution of the components in the liquid phase is more rapid.

In modeling the process, we notice that the crystallization rate of Al strongly depends on the concentration of Ge dissolved in the Al crystals. The crystallization stops if the Ge concentration exceeds the solubility limit. The Ge atoms need a certain amount of time to diffuse through the Al crystals and precipitate onto the Ge aggregate that grows inside, which is why we call the growth of the Al crystals diffusion limited. In the following we build a model of Al crystallization that couples the growth of the Al crystal and the Ge aggregate by a diffusion process.

We model the amorphous Ge:Al alloy by using a square lattice in which each site with coordinates x and y represents an atom of either Ge or Al with probabilities p and $1 - p$, respectively, where p is the Ge concentration in the amorphous phase. Initially, the interface between the crystalline Al and the amorphous phase is supposed to be a straight line $y = 1$; i.e., the lattice sites, where $y > 1$, belong to the amorphous phase and the lattice sites, where $y = 0$ (forming a straight line), belong to the Al crystalline phase. The lattice sites, where $y < 0$, represent a Ge aggregate that starts to grow within the Al crystals.

The sites in the Al crystal are characterized by a certain concentration c of the dissolved Ge. The concentration is assumed to be a continuous variable that varies from 0 for pure Al crystal to 1 for pure Ge.

The diffusion of Ge inside the Al crystal is modeled by the diffusion equation with diffusion coefficient D ,

$$\partial c / \partial t = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right), \quad (1)$$

which is discretized on the same square lattice with cell size Δx and time step Δt . We assume two different dynamical boundary conditions on the boundaries with amorphous phase and with Ge aggregate. We choose reflecting boundary conditions on the amorphous phase interface. We assume that the crystallization velocity depends on the concentration of Ge dissolved in the Al crystal. If the concentration of Ge is larger than the solubility limit c_ℓ , the crystallization stops. Thus we assume that the crystallization velocity is equal to some constant v if $c < c_\ell$ and is zero otherwise [9].

At each time step Δt , we examine all cells on the amorphous side of the crystalline-amorphous interface, and we incorporate them into the Al crystal with a probability $f = v\Delta t / \Delta x$. The Ge concentration of the newly incorporated cell is set at 0 (if it contained Al in the amorphous phase) or 1 (if it contained Ge).

The growth of the Ge aggregate is simulated by the flow of Ge through the Al-Ge interface with an absorbing boundary $c = 0$ on the Ge side. For each cell of the Al crystal that has at least one common edge with the aggregate, we calculate the total amount of Ge that penetrates through its edges into the Ge aggregate. Once this quantity exceeds a certain threshold value n , the cell is incorporated into the Ge crystal. This value n characterizes the number density of the Ge aggregate, $n = 1$, if one lattice cell of area Δx^2 contains one Ge atom.

In order to understand the mechanism of experimentally observed avalanche behavior, we simulate the influence of various parameters of the model on the dynamics of the amorphous interface propagation. We found that, when p is in the range of 0.45 to 0.60, the solubility of Ge is $c_\ell = 0.1$ and, when $D/v \leq 0.3\Delta x$, the interface propagates in avalanches (see Fig. 2, which shows the interface at two different moments). A growth of the avalanche is seen at the center (marked “A”) while the rest of the interface is blocked. The model is consistent with the invasion percolation-type [10,11] of growth process.

Assuming a random distribution of Al and Ge in the amorphous matrix, Al-rich and Ge-rich clusters are expected. As the growing Al crystal is supersaturated by Ge, the local velocity of the interface slows down. The Al-rich clusters in the amorphous phase are the preferred growth regions, since the local growth in these areas reduces the concentration of Ge (unblocking a larger fraction of the cells on the crystalline interface), and hence further increases temporarily and locally the

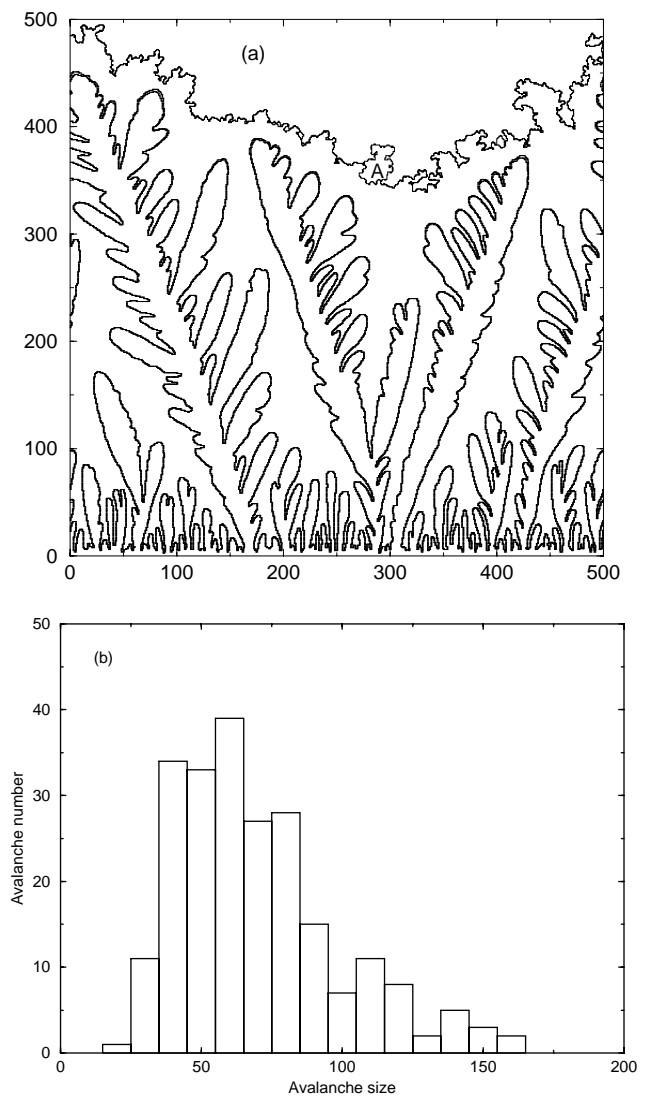


FIG. 2. Results of the model. (a) Time evolution of the crystalline-amorphous interface for $p = 0.45$, $c_\ell = 0.1$, and $D = 0.1v\Delta x$. The two positions of the interfaces are shown, separated by $\Delta t = 1000$ time steps of the simulation. The Ge branches are seen behind. While propagation of the interface occurs at the center (marked as A), the rest of the interface is completely blocked. Note that it is possible to compare the details down to the pixel level ($\Delta x = 1$). (b) The distribution of avalanche sizes in the model for $D = 0.3v\Delta x$.

average velocity of interface propagation. However, the propagation of the interface through Ge-rich areas is diffusion limited, since the dissolving of Ge raises the Ge concentration above the solubility limit and thus blocks the growth of the Al crystals. Finally, the interface completely stops until the excess of Ge atoms diffuses toward the Ge crystalline aggregate. Such “traffic jams” lead to local fluctuations of the interface velocity. Thus the model shows that it is the diffusion of Ge in the Al crystalline phase—not the nucleation events of Al in the amorphous phase—that leads to the large avalanches in the interface propagation.

We find that the avalanche sizes depend mostly on the diffusion rate D —the faster the diffusion rate (when compared to the crystallization rate v), the smaller the avalanche size. Thus at high diffusion rates ($D > 0.3v\Delta x$) the interface propagates smoothly with only small regions of the interface that are completely stopped at any given moment of time. This happens because the Ge concentration quickly equilibrates along the interface. At low diffusion rates, large portions of the interface are completely stopped for long periods of time—allowing excess Ge to diffuse away from the interface and into the Ge aggregate. Once the growth of Al crystals is initiated at some point on the interface, the Ge concentration at this point drops and the growth continues until the concentration exceeds the threshold c_ℓ due to the diffusion of Ge from regions with higher concentrations and the solvation of the Ge from the amorphous phase.

Finally, we compare the distribution of avalanche sizes in the model and in the experiment. In order to do this, we must develop a definition of “avalanche” in the model that is sufficiently similar to the definition of an experimentally observed avalanche, which is related to the spatial and temporal resolution of the video. An experimentally observed avalanche is defined as a connected area with a velocity of interface propagation that is several times larger than the average crystallization velocity. Accordingly, we define an avalanche in the model as a connected area with a local velocity of interface propagation 2 times larger than the average velocity. In Fig. 2b we present the distribution of avalanche sizes for the case $D = 0.3v\Delta x$, which has the same general features as the experimentally observed avalanche distribution, including the presence of a characteristic size and the lack of small avalanches. Small avalanches are invisible in the experiment since they all coalesce and contribute to apparently continuous slow “creeping” of the interface.

Our model is similar to invasion percolation and hence we can expect the distribution of the avalanche sizes s to be a power law $P(s) \sim s^{-\tau}$ for small s and an exponential for $s > S_0$, where S_0 is a characteristic avalanche size [11], which depends on the parameters of the model, such as $D/(v\Delta x)$. Indeed, if we measure the distribution of avalanches in the model without imposing the condition on their velocity, we obtain a power law distribution with an exponent $\tau \approx 1.5$, which is in good agreement with the theoretical prediction of [11], with an exponential decay for $s > S_0$. This power law distribution has an extremely large number of small avalanches with slow velocities, and hence is undetectable in the experiment. However, the fraction of the total area of a crystal, covered by these undetected small avalanches, is negligible since it scales as $s_0^{2-\tau} \approx s_0^{0.5}$, where s_0 is the left cutoff of the experimentally observed distribution. This is consistent

with the experimental observation, that the slow creeping of the interface is negligible in comparison to fast jumps produced by large detectable avalanches. On the other hand, we find that the characteristic size of the avalanches, S_0 , as well as the average avalanche size, \bar{s} , decrease with the increase of the relative diffusion rate $D/v\Delta x$.

In conclusion, we have quantified crystal growth using *in situ* time-resolved electron microscopy. We find a non-continuous mode of interface propagation, with a characteristic avalanche size scale of 10^5 atoms. Computer simulations of the process indicate that avalanches are caused by local inhomogeneities in the amorphous phase, and that the average size of avalanches is determined by the rate of diffusion.

We thank A. Brokman, S. Havlin, and A. Bourret for critical discussions, and the US-Israel Binational Science Foundation Grant No. 94-00333 and the NSF for support.

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