The Kinetic Analysis of Phase-Change Data-Storage Media

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Abstract: The analysis of phase-change kinetics is of clear importance for the optimization of chalcogenide media for data storage, as well as for understanding the limits of performance.   Published work on phase-change media mostly relies on analyses developed for phase transformations in bulk materials.   Such analyses have problems when applied to thin films, and still more when applied to constrained volumes and to cases with extreme temperature gradients and extreme rates of change of temperature.   The limitations of conventional kinetic analyses are examined, as are approaches to making the analyses more relevant to phase-change media.

1.   Introduction

The reversible phase change between crystalline and amorphous (glassy) states in chalcogenide-based thin films is of importance not only in optical memory discs (such as CD-RW) but also non-volatile RAM applications, and is being studied in particular examples such as Ovonic Unified Memory (OUM).   Understanding the kinetics of the phase changes has an important role in optimizing the performance of current data storage technologies as well as in developing new ones.   It may also help to establish the ultimate limits on performance (storage density, write times, read times, error rates, cyclability and shelf life).

Amorphization is accomplished by melting (whether by laser heating of optical discs or electrical Joule heating in OUM), and subsequent rapid quenching.   Melting starts readily without a nucleation barrier and its spatial extent is determined by the imposed temperature profile.   Crystallization occurs on less severe heating;   it is more complex and is the focus of interest in modelling transformation kinetics.   It is also of direct importance in limiting the speed of over-writing.   Crystallization can involve the stochastic process of *nucleation* as well as *growth*.   Modelling of these processes is particularly challenging because of the extreme conditions involved: high heating and cooling rates, steep temperature gradients, small volumes.   These conditions are also the major motivation for modelling, as direct experimental probes are difficult.   Modelling, if further developed, would usefully complement the excellent progress which has been made in direct measurement, for example using a static tester [1, 2].   Already, kinetic descriptions such as TTT (time-temperature-transformation) curves, are being considered in the design of phase-change conditions;   an example is the use in OUM of a ramped temperature in the "set" pulse to allow for spatially non-uniform temperature in the memory cells [3].

Modelling of solidification is well developed for conventional solidification in metallurgical processing.   Although the conditions in phase-change storage and in conventional solidification are extremely different (as will be explored in the next section) the fundamental atomic-level processes are the same.   Since quantitative, predictive modelling is so well established for metallurgical processing (and is standard in industrial practice), it is wise to consider what can be learned from it for application in phase-change media.

2.   Modelling of Conventional Solidification

Comprehensive computer modelling of solidification must include, among many factors, macromodelling of fluid flow and heat transfer, and micromodelling of phase nucleation and growth.   Fluid flow is unlikely to be important in phase-change media, even though material flow has been noted in optical discs.   Thermal modelling may pose difficulties, particularly for the steep temperature gradients in phase-change media, but generally involves standard techniques.   Our focus is therefore on nucleation and growth.

As demonstrated extensively, e.g. [4], quantitative models have been developed for the many aspects of growth in the solidification of metallic alloys.   These include cellular and dendritic morphologies and two-phase eutectic growth.   The main obstacle to fully predictive modelling is lack of knowledge of nucleation [5].   The nucleation law employed in most modelling is obtained by fitting, rather than from independent analysis.   In special cases there has been progress.   In the solidification of aluminium and its alloys, it is almost universal to add nucleant particles to the melt to refine the solidified grain structure.   A new analysis of grain initiation on these particles has permitted quantitative predictions of the microstructures arising from this grain refinement process [6].

When a nucleation law (obtained by fitting, or independently) is adopted, it can be used in microstructural modelling. An example is shown in Fig. 1, generated by cellular-automaton (CA) modelling, which has been extensively developed and tested for metallurgical processing [7, 8]. A grid is defined in which solidification proceeds from cell to cell. Both nucleation and growth are simulated in the same CA grid, within which the cell size must be somewhat less than the spacing between the crystal tips for reliable modelling of dendritic growth. Thermal diffusion lengths are typically much larger than the crystal size, so that heat flow can be analysed (usually with a finite-element algorithm) with a mesh much coarser than the CA grid. In the combined cellular-automaton finite-element (CA-FE) model the thermal computation is fully coupled with the latent heat released in the CA cells and with changes in specific heat.
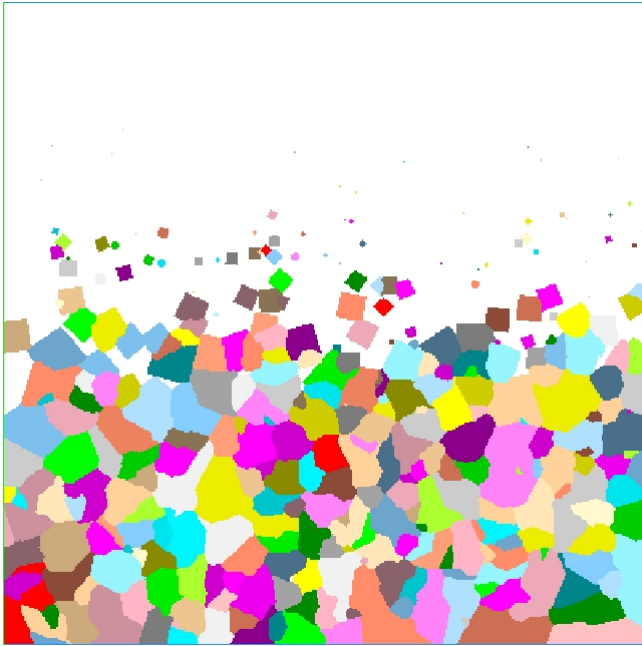

Fig. 1. A two-dimensional CA-FE microstructural simulation showing the grain structure in an Al - 3.5wt.% Mg alloy during solidification at ~10^{-3} m s^{-1} in a temperature gradient of 10^4 K m^{-1}. The area shown represents 1 mm^2. The temperature decreases from top to bottom, and the featureless area at the top is the liquid ahead of the solidification front. (courtesy T. E. Quested)

The microstructure in Fig. 1 is *equiaxed*. Crystals are nucleated in the liquid ahead of the main growth front and grow sufficiently to block the advance of the crystals at the front. If there were no nucleation of crystals ahead of the main front, or if their development were insufficient, solidification would proceed only by growth of existing crystals giving a microstructure of *columnar* crystals. In the metallurgical literature, there has been much analysis of the so-called *columnar-to-equiaxed transition* [9]. The transition for a given material can appear quite sharp as solidification conditions are changed. Equiaxed solidification is favoured by high solidification velocity and low thermal gradient. Equiaxed solidification is analogous to so-called *nucleation-dominated* crystallization [10], and columnar solidification to *growth-dominated* crystallization in phase-change media.

Table 1 presents a crude comparison of typical conditions in metallurgical solidification and phase-change crystallization. The extreme differences force significant differences in approach if modelling of the kind in Fig. 1 is attempted for crystallization of phase-change media.

Table 1. Cooling conditions in metallurgical casting compared with those after amorphization or crystallization pulses in phase-change media.

	Cooling Rate (K s^{-1})	Temp. Gradient (K m^{-1})	Crystal Front Vel. (m s^{-1})	Melt Volume (m^3)
metallurgical solidification	1 to 10	~10^4	~10^{-3}	10^{-5} to 30
phase-change crystallization	~10^{10}	10^9 to 10^{12}	1 to 100	10^{-21} to 10^{-20}

3. Nucleation

The modelling of grain refinement in aluminium alloys, cited above [6], is based on there being no strict nucleation barrier on the added nucleant particles.   For crystallization of phase-change media, in contrast, the delays (incubation times) imply that there can be a nucleation barrier.   The crystallization speed and crystal size are dependent on: the choice of dielectric layers bounding the chalcogenide layer [11];   the presence of acceleration layers [12];   and the thickness of the chalcogenide layer [12, 13].   Such dependences clearly show that the nucleation must be *heterogeneous*, i.e., not completely intrinsic to the chalcogenide itself.   The standard model for heterogeneous nucleation takes the nucleus to be in the form of a spherical cap on a catalytic substrate.   In this case the work of forming a critical nucleus (the nucleation barrier) can be much lower than for homogeneous nucleation, but it remains true that nucleation involves the development of stable clusters through forward and backward reactions in which individual atoms join or depart.   If the cluster size distribution (from the smallest up to the critical size) is in steady state, then nucleation events occur at a constant rate.   The dynamics of the cluster size distribution have been extensively modelled [14, 15].   At the cooling rates in conventional metallurgical processing, the steady state is readily maintained.   With rapid solidification techniques, such as melt-spinning giving cooling rates of 10^5 to 10^6 K s^{-1}, the deviations from the steady state are large (Fig. 2, [16]), and must be even more so at the even higher cooling rates experienced by phase-change media.   Transient nucleation effects could contribute to incubation-time effects of the kind seen in static testing [1].   They impede nucleation and thereby promote glass formation.   They must also play a role in crystallization.   At the heating and cooling rates involved in phase-change recording it is inconceivable that nucleation could be in steady state.
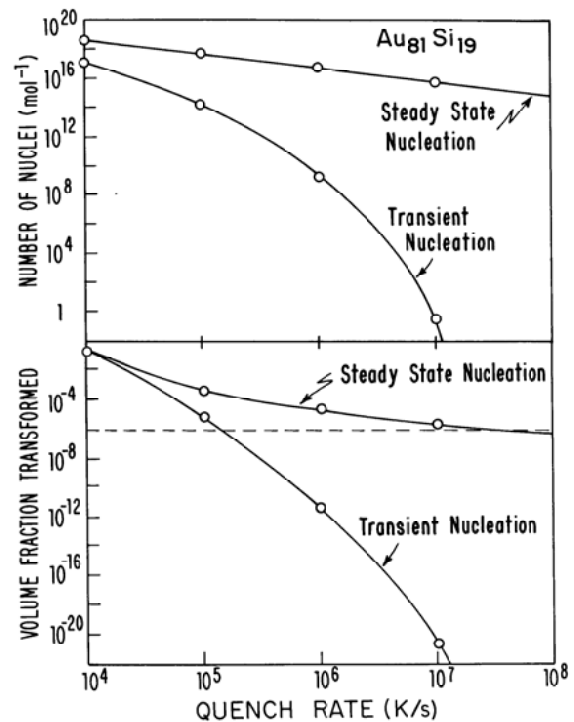

Fig. 2.   The number of nuclei (a) and transformed volume fraction (b) calculated for quenching the marginal metallic glass-forming alloy $Au_{81}Si_{19}$ (at.%) from the equilibrium liquid state at various rates, assuming steady state or transient nucleation.   (from [16])

The numerical modelling of cluster development in terms of addition or subtraction of individual atoms becomes computationally onerous if it is continued up to the final crystal size [17].   It is much more efficient to use the numerical modelling only up to cluster sizes just beyond critical.   After that, growth is deterministic, and its rate can be evaluated analytically [16].   Such an approach was used to calculate the behaviour shown in Fig. 2.   It is important to note that the growth rate does not take its macroscopic value because of the high curvature of the solid-liquid interface at small crystal sizes.

The small melt volume and lifetime greatly lower the probability of nucleation. As shown in single-shot reflection experiments [1], nucleation can even fail to occur. As data-storage densities increase and mark sizes decrease, crystallization (erasure) is likely to have to rely on growth from the surrounding crystalline material.

4. Growth

The likely growth modes in phase-change crystallization are much simpler than the variety found in metallurgical solidification. The high rates of crystallization which are imposed, and which are required for a successful technology, force the crystallization to be *congruent* [3]. There can be little or no partitioning and no development of two-phase eutectic microstructures. The small scale and steep temperature gradients do not permit the development of cellular or dendritic morphologies. Even though long-range solute diffusion is not involved, the processes at the crystallization front involve diffusive atomic jumps. The growth is still described as *diffusion-limited* to distinguish it from the *collision-limited* growth associated with pure metals [18]. Collision-limited growth is potentially so rapid that it would not permit amorphous phase formation even at extreme cooling rates [18]. Figure 3 shows the very different temperature dependences of homogeneous nucleation and growth rates for a typical metallic glass-forming system [19]. It is known that crystallization of phase-change media, for example during initialization, can occur from the liquid or the glassy state [20, 21]. Figure 3 shows that near the glass-transition temperature T_g nucleation rates are expected to be low. At higher temperature the rates of nucleation and growth accelerate and the greater rate of heat release can give rise to explosive crystallization. Such effects can be suppressed, however, by rapid external heat extraction. The cooling rate contours in Fig. 3 show that at the cooling rates typical in phase-change media, explosive crystallization would be suppressed. It is also suppressed by the limited volume in which crystallization can occur.
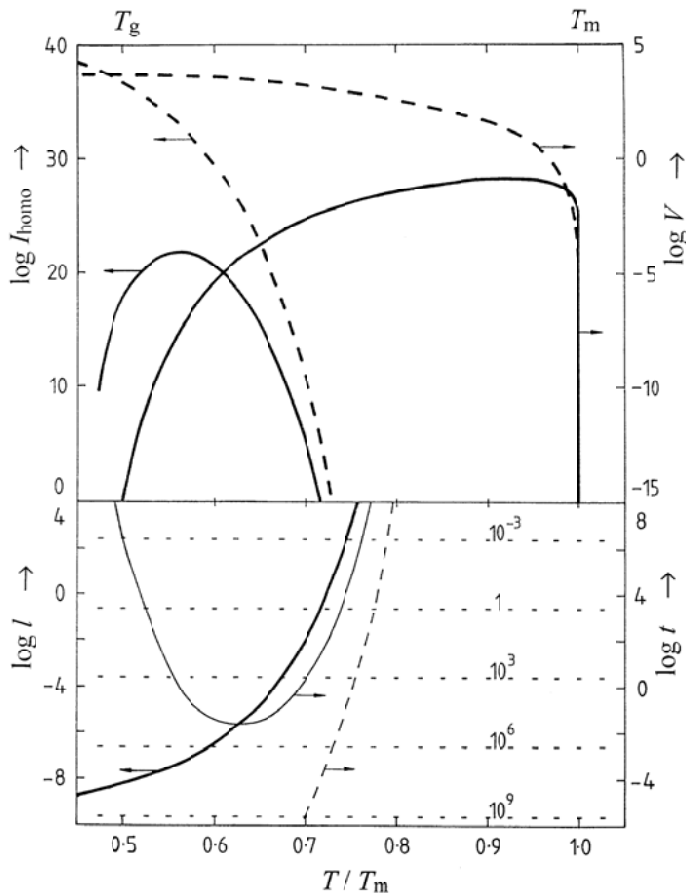

Fig. 3. Calculated crystallization kinetics for a typical metallic glass-forming alloy showing diffusion-limited (solid lines) and collision-limited (dashed lines) kinetics. Shown are the $\log_{10}$ of: I_{homo} (homogeneous nucleation rate, $m^{-3} s^{-1}$), V (crystal growth rate, $m s^{-1}$), l (grain size $(V/I)^{1/4}$, m) and t (solidification time, $l/2V$, s). The grain size is the same for both types of kinetics. The horizontal lines are labelled with cooling rates in $K s^{-1}$. If the solidification time falls below these lines, the liquid will heat up (*recalescence*) and there may be explosive crystallization. (from [19])

The temperature gradients in phase-change media are extreme, much larger than in conventional processing. This can give rise to *thermomigration* would normally be negligible. The chemical potential of different elements varies differently with temperature, and thus temperature gradients can in principle give composition gradients. Research is needed on such effects, in particular to assess whether they could limit cyclability. Cyclability can be limited by the thermomigration of voids (through the Marangoni dependence of surface tension on temperature) if they are present [22]; the voids migrate towards the hottest zone over repeated cycles.

In conventional solidification, the liquid undercoolings can be very small (<< 1 K). In such a case, curvature of the solid-liquid interface can have very significant effects on the undercooling and on the resulting microstructure. It might be expected that the smaller length scales involved in phase-change recording could similarly have strong effects. For example, if it were possible to have an amorphous mark of 20 nm diameter [23], its interface with the surrounding crystalline medium would necessarily be very curved. This curvature, with a typical solid-liquid interfacial energy, would raise the effective melting point of the crystal by approximately 20 K. In conventional solidification such a change could have an enormous effect. In the phase-change application, however, this curvature effect would be negligible, swamped by the large temperature changes in small volumes.

5. Transformation Kinetics

For metallurgical solid-state transformations, such as the growth of pearlite in austenite, the kinetics are often described using the Johnson-Mehl-Avrami (JMA) equation [24]. This has its origin in the derivation of volume fraction transformed V_f from an extended volume fraction V_f^{ext} which would apply if there were no impingement of transformed volumes:

$$V_f = 1 - \exp\left(-V_f^{ext}\right) \tag{1}$$

As V_f^{ext} goes from 0 to infinity, V_f goes from 0 to 1. The extended volume fraction is readily calculated from nucleation and growth rates, and is proportional to $time^n$ (where n is the Avrami exponent). Equation 1 applies when nucleation is randomly distributed in space; this condition is very unlikely to be satisfied in the crystallization of phase-change media, for which the total volume involved in crystallizing can be comparable with the volumes of individual crystals. If the JMA analysis is to be applied in a given volume element (for example in a finite-element calculation) then the volume element should be very large compared to the scale of the crystallization microstructure; again, this condition is rarely if ever met. It may be better to use stochastic modelling of realistic microstructures, as shown in Fig. 1. Modelling of this kind has already been applied to the crystallization of phase-change media [13].

6. Electromigration

Potential thermomigration effects were mentioned above. In OUM in which the melting and crystallization are effected by electrical Joule heating, it would be worthwhile to investigate possible *electromigration* effects. Electromigration, in which atomic diffusion is biased in the presence of an electrical current, giving a net atomic flux, is a major source of reliability problems in integrated circuits [25]. The problems arise when the atomic flux is not uniform, caused by temperature gradients, or by changes in conducting material (for example between tungsten and aluminium at vias). As there are steep temperature gradients and materials interfaces in OUM-type devices, it seems reasonable to expect electromigration-induced stresses to arise. On the other hand, conventional electromigration testing shows that such stresses give rise to damage only if a critical length scale is exceeded. The small scale of OUM memory cells may preclude the development of damage.

7. Conclusions

Despite the extreme transformation conditions in phase-change media (high heating and cooling rates, steep temperature gradients, and small volumes), it is possible to analyse the kinetics in terms of crystal nucleation and growth. However, standard modelling techniques such as are applied for quantitative microstructure prediction in metallurgical casting, must be substantially modified. With presently foreseeable technology, the phase change itself does not appear to limit the scaling down of memory cell size.

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