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ON DENSE BRANCHING PHASE SEPARATION

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Recently Deutscher and Lareah[1] discovered a new mode of phase separation in thin films of Al/Ge alloys. They observe the growth of circular "colonies" whose densely packed appearance has been called "dense branching morphology"[2]. The colonies consist of a highly branched starlike "island" of polycrystalline Ge inside a "lake" of monocrystalline Al which is only slightly larger than the Ge island. Thus the Al forms a thin but essentially uninterrupted rim around the Ge peninsulas. The whole colony is embedded in the amorphous phase having an overall composition of 40% Al and 60% Ge. As these colonies grow into the metastable amorphous surrounding they preserve their more or less circular shape.

This immediately raises the question why on the one hand the Al/Ge-interface shows an instability, while on the other the Al/amorphous boundary does not. We investigate this question first. We then present the theoretical description of the new growth morphology. We outline the solution of our equations and indicate how a unique growth velocity is selected. We finally compare our results with experiment.

We first turn to the stability problem for the Al/amorphous interface: During ordinary solidification from a melt the excess foreign atoms have to be cleared away from the solid/liquid interface by chemical diffusion. If this diffusion process has to occur into the metastable phase and over large distances it will be more effective if the interface area is increased. This leads to the Mullins-Sekerka instability and a dendritic morphology for the growing crystal[3].

The MS-instability is more formally derived from the diffusion equation together with two boundary conditions for the moving interface. The first boundary condition demands energy conservation across the boundary while the second condition is a statement of thermodynamic equilibrium including the Gibbs-Thomson correction due to surface tension. A steady state solution is given by a flat interface moving with velocity ϑ into the metastable phase in front of which the diffusion field decays exponentially. One then adds a small perturbation ζ to the moving front

$$\zeta(\vec{r}_\perp,t) = \zeta_k \exp\,(i\vec{k}\cdot\vec{r}_\perp + \omega t)$$

where $\vec{r}_\perp$ denotes the position in the plane perpendicular to $\vec{v}$. The problem becomes to determine the amplification rate ω for a perturbation with wavevector $\vec{k}$. The sign of ω will decide whether the perturbation is enhanced or suppressed. Carrying out the linear stability analysis along the lines of Langer[3] one obtains

$$\omega = -\frac{D}{2\xi^2} + D\left(\frac{1}{\xi} - 2d_0k^2\right)\left(\frac{\omega}{D} + k^2 + \frac{1}{4\xi^2}\right)^{1/2}$$

as the relation between ω and k. In the above relation $\xi = D/v$ is the diffusion length and d_0 is the so called capillary length which is determined by the surface tension. The relation is valid for the symmetric model, i.e. when the diffusion constant D in the solid equals that in the melt. The usual argument[3] proceeds with two assumptions: 1. $k\xi >> 1$ assumes that the diffusion length is very large (usually macroscopic). 2. $\omega << Dk^2$ assumes that the time scale for diffusing a distance on the order of the wavelength of the perturbation is much shorter than the time scale on which growth occurs (quasistationarity). With these two assumptions one finds the MS-instability for wavelengths above $\lambda = (2d_0\xi)^{1/2}$.

What distinguishes our case from solidification in a melt is the fact that the diffusion constant in the amorphous phase is much smaller than in a melt. Thus ξ is no longer macroscopic and we have to consider the case $k\xi << 1$. At the same time the quasistationarity assumption breaks down because the term ω/D under the root can no longer be neglected. One finds that $\omega=0$ at $k=0$ while $\omega = -D/2\xi^2 = -v^2/2D$ at the wavelength governing the MS-instability. Thus in this case perturbations are damped out. For very long wavelengths the damping becomes weak. This effect can also be observed in the experiment.[4]

We now proceed to develop a set of equations describing the growth. Compelled by the experimental evidence we arrived at the following central features of our description: 1. The dominant diffusion is that of atomic Ge backward from the Al/amorphous interface into the crystalline Al. 2. Atomic diffusion in the amorphous phase is very slow compared with the crystalline phase. 3. Nucleation and growth of Ge crystallites occurs only at the interface between Al and Ge. 4. Nucleation of Al crystals in the amorphous phase is much more frequent than that of Ge but still rare; it controls the initiation of new colonies. Of these assumptions the first one is at the heart of our understanding. It stems from the observation that the Al/Ge interface is separated from the amorphous phase by an Al rim and can only grow if Ge atoms diffuse across this rim. We argue that the interplay between the Al/amorphous boundary and the Al/Ge boundary which act respectively as source and sink for Ge atoms sets the length scale of the problem. Note that the length scale is strongly temperature dependent.[1]

To approach the problem mathematically we concentrate on the smooth Al/amorphous boundary and describe the highly irregular Al/Ge interface in an averaged fashion. We replace the local concentration of atomic Ge by its radial average c(r) and that of crystalline Ge by its radial average ρ(r). Then we have

$$\frac{\partial c}{\partial t} = D_L\,\nabla^2 c - \frac{\partial \rho}{\partial t} \qquad \text{(1a)}$$

on the "left" inside the Al and

$$\frac{\partial c}{\partial t} = D_R\,\nabla^2 c \qquad \text{(1b)}$$

in the amorphous phase on the "right" of the interface. D_L resp. D_R is the diffusion constant on the left resp. right. At the interface on has $c = c_L$

on the Al side ($r=R_-$) and $c = c_R$ on the amorphous side ($r=R_+$). Taking excluded volume effects into consideration in these equations somewhat complicates the analysis but does not change its essential features. We describe the growth process in its simplest form as

$$\frac{\partial \rho}{\partial t} = Bc\rho \tag{2}$$

The phenomenological rate constant B describes the growth of the branched Ge structure and thus incorporates nucleation and growth of Ge crystallites. At the Al/amorphous interface, $r = R(t)$, the diffusion field must obey mass conservation:

$$\frac{d}{dt} R(t)\left(\Delta c + \rho(R) \right) = D_L \frac{\partial c}{\partial r}\bigg|_{r=R_-} + D_R \frac{\partial c}{\partial r}\bigg|_{r=R_+} \tag{3}$$

Here $\rho(R)$ is a small seed concentration of crystalline Ge at the boundary which is seen in the experiment. $\Delta c = c_R - c_L$ denotes the discontinuity in the concentration across the interface (miscibility gap).

The ramified Al/Ge boundary close to the Al/amorphous boundary acts as a sink for the diffusing Ge and from Eq. (3) this implies a finite concentration gradient and thus a finite velocity for the moving front. Searching for constant velocity profiles we write

$$c(r,t) = c_0 \; f(z) \qquad \text{resp.} \qquad \rho(r,t) = c_0 \; g(z) \tag{4}$$

where $R = vt$, $z = (r-R)/\xi$, c_0 is the concentration of the in the amorphous phase and $\xi = D_L/v$ is the basic length scale in the problem. For sufficiently long times ($v^2t/D_L \gg 1$) the curvature of the interface can be neglected and one obtains a closed nonlinear equation for f [5]

$$f' + f'' = \beta f \; (1 - f - f') \tag{5}$$

with the boundary conditions

$$f(-\infty) = f'(-\infty) = 0 \tag{6a}$$

$$f(0) = c_L/c_0 \tag{6b}$$

$$f'(0) = 1 - c_L/c_0 - \varepsilon \tag{6c}$$

where $\beta = c_0 B D_L/v^2$ is a dimensionless control parameter and $\varepsilon = g(0)$ is the small seed concentration at the interface introduced in Eq. (3). We display the solutions to Eq. (5) in f-f'-space in Fig. 1 . Trajectories fulfilling the boundary conditions at $z=-\infty$ emerge from the origin with a slope $f'/f = 1/\zeta = [-1 + (1+4\beta)^{1/2}]/2$. The straight line $1-f-f'=0$ is a separatrix. The boundary condition Eq. (6c) determines a straight line parallel to the separatrix. If we choose a value for β we must follow the associated flow line starting from (0,0) until it intercepts this straight line and read off the corresponding value $f(0) = c_L/c_0$. This determines β and thus v as a function of c_L (see inset of Fig. 1).

After demonstrating how the boundary conditions effect a velocity selection we compare the results with experiment.[4] The growth velocity is found to be constant as predicted. For slow velocities, i.e. $\beta \gg 1$, one derives the relation $v \approx (c_L/c_0)D_L/\xi\zeta$. It has been checked experimentally by comparing the temperature dependence of $D/\xi\zeta$ with that of v and seems to be in quantitative agreement. If the temperature dependence of v were given by that of D_L one would expect a temperature independent length scale. Instead we have $v \propto (BD_L)^{1/2}$ which shows that both B and D_L contribute. In a first check

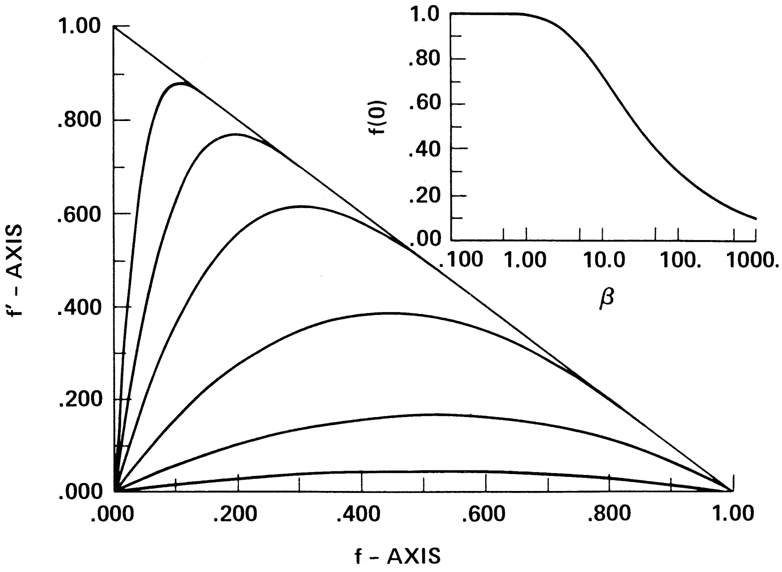

Fig. 1 : Trajectories fulfilling the boundary conditions at $z=-\infty$ for selected values of β (β = .2,1,5,25,100,500).
Inset: Dependence of $f(0)=c_L/c_0$ on β for trajectories fulfilling all boundary conditions with ε = .001

this relation has been found consistent with the values of the activation energies of the quantities involved.[4] In addition the values of c_L and c_R have been checked against the Al/Ge phase diagram.[5] In conclusion we have shown that our simple analysis agrees qualitatively with all known experimental facts. Further theoretical work has to concentrate on a microscopic model for the nucleation and growth process. More detailed experimental data are needed to explore the limits of quantitative agreement.

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REFERENCES

1. G. Deutscher and Y. Lereah, Physica 140A (1986), 191
2. E. Ben-Jacob, G. Deutscher, P. Garik, N. Goldenfeld and Y. Lereah, Phys. Rev. Lett. 57 (1986), 1903
3. J.S. Langer, Rev. Mod. Phys. 52 (1980), 1
4. G. Deutscher and Y. Lereah, preprint
5. S.Alexander, R.Bruinsma, R.Hilfer, G.Deutscher and Y.Lereah, preprint