Massachusetts Institute of Technology

Department of Materials Science and Engineering

77 Massachusetts Avenue, Cambridge MA 02139-4307

3.21 Kinetics Processes in Materials—Spring 2006

Examination #3—Instructor's Solution

May 17, 2006

9:30–10:55 A.M.

This is a *closed book* examination. Calculators may be used when necessary.

Please answer the questions directly on the exam pages. If you require more room, use the backs of the facing pages.

There are three questions on this examination. Apportion your time accordingly.

Keep your answers short and to the point. When appropriate, include sufficient information to indicate your reasoning. This will enable us to award appropriate credit even if you do not answer the question completely.

Good luck!

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Please write your name here

1. Figure 1 is a transmission electron micrograph of the transformation morphology observed when an ordered FeAl crystal with the CsCl structure is cooled into a miscibility gap and transformed there. The micrograph is a dark-field image using a superlattice reflection, so that bright regions are ordered and higher in Al content, and dark regions are disordered and lower in Al content. The long curved dark line is an antiphase boundary, and can be ignored in this problem.
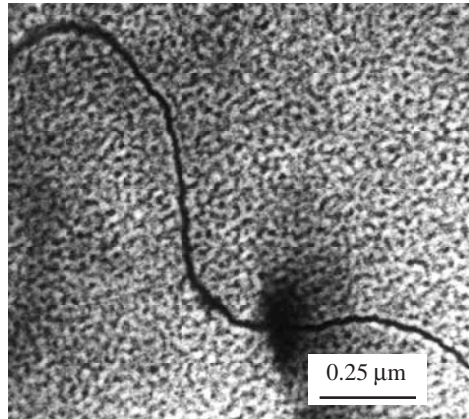

0.25 μm

Figure 1: Microstructure in phase separated Fe–24 at.% Al alloy.

(a) Considering the morphology and characteristic length scale of the microstructure, the likely mechanism of phase separation is spinodal decomposition. Why is it somewhat surprising that this alloy transforms by spinodal decomposition?

Solution. The customary view that crystalline solutions will "order" or "phase separate" based on the near-neighbor bond preferences would make one believe that ordering and spinodal decomposition are "opposite" sorts of behavior and in a given system the sign of the enthalpy of mixing would determine if a system would order (A–B bonds preferred) or phase separate (A–A and B–B bonds favored). In the Bragg-Williams model we studied, we found that the sign of the parameter W (Ω in the regular solution model) determined the behavior. With this oversimplified picture, it is indeed surprising that an Fe–Al alloy with CsCl order would be unstable with respect to spinodal decomposition. (The Bragg-Williams model will give this behavior under certain conditions if both first and second neighbor interactions are considered.)

(b) Measurements of elastic constants in Fe-Al alloy single crystals show them to be highly elastically anisotropic. Considering the observed microstructure and your knowledge of spinodal decomposition, why is this surprising?

Solution. The morphology of spinodal decomposition in crystalline materials is largely determined by the elastic energy term $2\alpha_c^2 Y$ and in most alloys the elastic constant Y varies with crystallographic orientation of the wave vector of decomposition, $\vec{\beta}$. Composition waves tend to grow fastest along elastically soft directions in elastically anisotropic alloys. Given that Fe-Al alloy elastic constants are highly anisotropic, the phase separated microstructure should be strongly aligned as in *KoM* Fig. 18.13(b).

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The unaligned spinodal structure observed in the figure would be expected for decomposition in an alloy that is elastically isotropic, or one that has very little change of lattice constant with composition.

(c) Measurements of the lattice constants of Fe–Al alloys over a range of compositions and temperatures show that the lattice constant increases with Al content in disordered alloys and that increasing long-range order actually decreases the lattice constant. Explain how this might explain the observed phase separated morphology in the micrograph.

Solution. The nonaligned morphology observed could result if the phase separated structure can form with essentially no change of lattice constant between the phases. The disordered phase has the lowest aluminum content and the lattice constant is smaller the lower the aluminum content. The ordered phase has the highest aluminum content and presumably a high degree of order. Although the lattice constant increases with composition in the disordered phase, ordering lowers the lattice constant, so it is likely that the system evolves the fields $\eta(\vec{r})$ and $c(\vec{r})$ in such a way to eliminate significant variation of lattice constant with composition in the two-phase mixture (disordered + ordered).

2. An orthorhombic crystal has three orthogonal low-energy surface orientations with values of excess free energy per unit area of $\gamma^{100} = 500$ mJ/m^2, $\gamma^{010} = 300$ mJ/m^2, and $\gamma^{001} = 100$ mJ/m^2. Assume that a fully-facetted critical nucleus forms with these interface orientations.

(a) Demonstrate that the shape of the critical nucleus will obey the relation

$$\frac{\gamma^{100}}{X} = \frac{\gamma^{010}}{Y} = \frac{\gamma^{001}}{Z} \tag{1}$$

where X, Y, and Z are the distances of the (100), (010), and (001) faces from the center of the critical nucleus, respectively.

Solution. Write an expression for ΔG for forming the brick-shaped particle with edge lengths x, y, and z:

$$\Delta G = xyz\Delta g_B + \gamma^{100}yz + +\gamma^{010}zx + \gamma^{001}xy \tag{2}$$

Determine the equilibrium shape by minimizing with respect to x, y, and z:

$$\frac{\partial \Delta G}{\partial x} = yz\Delta g_B + \gamma^{010}z + \gamma^{001}y \tag{3}$$

$$\frac{\partial \Delta G}{\partial y} = xz\Delta g_B + \gamma^{100}z + \gamma^{001}x \tag{4}$$

$$\frac{\partial \Delta G}{\partial z} = xy\Delta g_B + \gamma^{100}y + \gamma^{010}x \tag{5}$$

Setting these derivatives equal to zero and denoting the critical sizes as $x_c = X$, $y_c = Y$, and $z_c = Z$ gives the desired relation

$$\frac{\gamma^{100}}{X} = \frac{\gamma^{010}}{Y} = \frac{\gamma^{001}}{Z} = -\Delta g_B \tag{6}$$

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(b) The shape of this critical nucleus is very different from a sphere which has the minimum surface area per unit volume enclosed. Rationalize the facetted shape of the critical nucleus in this case in terms of the surface energy anisotropy.

Solution. A spherical shape will have smaller surface area than the fully-facetted brick-shaped particle of equivalent volume. Even though the brick has a larger surface area, the total surface free energy is made low by forming the critical nucleus with its largest faces in the orientation with the lowest surface free energy (i.e., (001) faces) and with its smallest faces in the orientation with the highest surface free energy (i.e., (100) faces).

3. Please identify which of the following statements is true or false. Give a brief justification for each answer. *Full credit requires concise, correct reasoning.*

(a) "Barrierless nucleation" of the β phase on α/α grain boundaries can occur when the interfacial energies are such that $\gamma^{\alpha/\alpha} \geq 2\gamma^{\alpha/\beta}$.

Solution. TRUE. When this condition is met the high-energy α/α grain boundary can be completely eliminated when the β phase forms on the boundary, as the energy of the two α/β interfaces that are formed by wetting will be less than the grain boundary energy. Without an interfacial energy barrier, there will be no energetic barrier to nucleation.

(b) A molten binary alloy may become constitutionally supercooled if the thermal gradient in the liquid ahead of the solid/liquid interface is sufficiently steep.

Solution. FALSE. Steep gradients in temperature actually *stabilize* the interface and promote "plane front" solidification. The thermal gradient must be sufficiently *shallow* in order to get constitutional supercooling (in which the actual temperature in the liquid falls below the temperature of the liquidus for the liquid's local composition).

(c) Antiphase boundaries are the most conspicuous microstructural feature in a material that has undergone a continuous ordering transformation.

Solution. TRUE. Continuous ordering occurs very rapidly and the main feature in the microstructure will be the APBs which are a special type of stacking fault between out-of-registry ordered domains. The characteristic length scale that evolves during ordering is that of the antiphase domains. The motion of these interfaces is capillarity driven and the kinetics are given by a solution to the Allen–Cahn equation.

(d) The time-cone method of describing transformation kinetics can be used to predict the grain size in a devitrified glass, knowing the grain nucleation rate J and the growth rate $\dot{R}$.

Solution. TRUE. The number of grains at the completion of the transformation is equal to the number of nucleation events that occur. The number of nuclei is given by the product of the nucleation rate J and the time-cone volume.