THE DYNAMICS OF PRECIPITATE EVOLUTION IN ELASTICALLY STRESSED SOLIDS—I. INVERSE COARSENING

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Abstract—The effects of elastic stress generated by a misfit between a particle and matrix on the morphological evolution of a two-phase microstructure have been investigated. The particles were allowed to evolve by the flow of mass through the matrix with the interfacial concentrations given by the elastic stress-modified Gibbs–Thompson equation. We find that neither the total elastic nor the total interfacial energy must decrease with time during the evolution of the particles. Two misfitting particles were never observed to be stable with respect to coarsening, in contrast to the predictions of energetic calculations using particles of fixed morphology. However, inverse coarsening, wherein a small particle grows at the expense of a large particle, was quite common in systems with more than two particles. This inverse coarsening process can, in some cases, be accompanied by a *decrease* in the total interfacial energy in the system. We also find that particles which are aligned along the elastically soft directions of the crystal can evolve by the flow of mass through the thin regions of matrix separating these particles.

1. INTRODUCTION

Ostwald ripening or coarsening is a late-stage phase transformation process which results in a dissolution of second-phase domains with high interfacial curvature at the expense of domains with low interfacial curvature. In this case, the total energy of the two-phase system is reduced via the increase in the size-scale of the second-phase particles which, in turn, implies that the total interfacial area in the system must decrease. This process occurs in many technologically important two-phase mixtures ranging from multiphase liquids to multiphase solids. However, there is strong experimental evidence to show that elastic stress has a profound influence on the precipitate evolution process in solids during coarsening [1–6].

Much of the theoretical work on the effects of elastic stress on coarsening processes has been based on calculations of the elastic energy of one or more particles of a chosen morphology, usually spheres, ellipsoids or cuboids [7–14]. On the basis of these calculations, a number of workers have claimed that elastic stress can induce inverse coarsening, wherein a small particle will grow at the expense of a large particle. For example, a bifurcation analysis due to Johnson [9] for the case of two elastically interacting spherical particles in an elastically inhomogeneous system has shown that if the particles are larger than a critical size, the energy of the system would decrease if the small particle were to grow at the expense of the large particle. Moreover, his analysis showed that

this two-particle system can be stabilized with respect to coarsening, as two particles of the same size can minimize the energy of the system. Similar results were obtained in dynamical descriptions of the coarsening process wherein the particles coarsen by mass flow and they were constrained to remain spherical [15–17]. However, the implications of fixing the particle morphology remains unclear. Onuki claimed that such a constraint can lead to qualitatively and quantitatively incorrect answers [18], whereas the more recent work of Abinandanan and Johnson shows quite reasonable results when the morphology of the particles is constrained to be spherical [19, 20]. Wang *et al.* have shown that inverse coarsening is possible in multiparticle systems in elastically anisotropic systems where the particle morphology is not fixed [21]. However, in contrast to the energetic calculations, stabilization of the system with respect to coarsening was not observed. More recently, inverse coarsening, but not stabilization, has been found in two-particle calculations in which the morphology of the particles are not fixed [22, 23].

It has been clear for some time that, within a fixed class of geometric shapes, elastic stress can induce symmetry breaking shape bifurcations in the morphology of a particle [24, 25]. Recent work, where the morphology of the particle is not fixed, has shown that shape bifurcations in the equilibrium shape of a particle can also occur [26, 27]. For example, in an elastically anisotropic system the equilibrium shape can change from a four-fold to a two-fold symmetric shape at a critical particle size [26]. The implications

of this shape bifurcation on the possibility of inverse coarsening, or the nature of the coarsening process itself, has not been investigated.

There are a number of theoretical approaches which can be used to examine the evolution of arbitrarily shaped particles in elastically stressed solids. One involves the solution of an elastic-stress-modified Cahn–Hilliard equation wherein the particle–matrix interface is taken to be diffuse [18, 21, 24, 28]. This approach has the advantage of not needing to track the location of the particle–matrix interface during the evolution process. Ising model-like approaches offer similar advantages [27, 29]. Here we will use an alternate approach where the interface is taken to be sharp, and thus the particles are large compared to the thickness of the interface. Continuum thermodynamics is used to determine the solute concentration at the interface [30–32]. By invoking the assumption of local equilibrium, these interfacial concentrations can be used as boundary conditions for a solution to the diffusion equation. The local interfacial velocities, and the evolution of the particles follow from this solution. This approach has been used in the past to examine particle evolution in elastically anisotropic [33] and elastically isotropic inhomogeneous systems [34].

Here we shall examine the coarsening process in systems with many misfitting particles in an elastically anisotropic solid in an effort to determine the mechanisms responsible for inverse coarsening. As past work has established a connection between the field equations and boundary conditions used to describe the evolution process and an energy which decreases upon solutions to these equations [32], we can examine the relative influence of elastic and interfacial energies on the morphological evolution process of a system of particles. Finally, we will compare our results to the classical approach where the particles have a fixed morphology.

2. FORMULATION

2.1. The free-boundary problem

We consider the evolution of coherent particles (β) in an infinite matrix (α). We do not constrain the shape of the β particles, but allow them to evolve in a manner consistent with the flow of mass in the system. We take the misfit between particle and matrix to be purely dilatational. This two-phase binary system is assumed to be elastically anisotropic with cubic symmetry and elastically homogeneous, i.e. elastic constants of both phases are identical. The lattice parameters of both phases and the elastic constants are assumed to be independent of composition. No traction is applied to the system at infinity. The total volume of particles will be constrained to be constant during the evolution process and the interfacial energy is assumed to be isotropic and independent of the interfacial strain.

The particles are assumed to evolve via the isothermal diffusion of mass at a sufficiently slow rate

that the quasistationary approximation for the diffusion field in the matrix holds. Thus, the concentration field in the matrix is given by a solution to

$$\nabla^2 C = 0, \quad (1)$$

where C is the mole fraction of component 2. Equation (1) must be solved subject to the composition at the particle–matrix interface as given by the stress-modified Gibbs–Thomson equation. By assuming local equilibrium, or negligible interfacial kinetics, the interfacial compositions are given by [30–32]

$$C^\alpha = C_i^\alpha + B^\alpha \left\{ \frac{1}{2} [\mathbf{T} \cdot \bar{\mathbf{E}}] - [\mathbf{T} \cdot \mathbf{E}] + \sigma \mathcal{K} \right\}, \quad (2)$$

where C^α is the interfacial concentration in the α phase, C_i^α is the equilibrium concentration in the matrix at a flat interface in the incoherent or stress-free state, $B = 1/[\rho \partial^2 G_m / \partial C^2 (C_i^\beta - C_i^\alpha)]$ in the designated phase with the second derivative of the molar free energy, G_m , evaluated at the equilibrium incoherent composition, ρ is the molar density of lattice points in the reference or stress-free state, $\mathbf{T}$ is the stress tensor, $\bar{\mathbf{E}}$ is the elastic strain tensor, $\mathbf{E}$ is the total strain tensor measured with respect to stress-free α , $\mathbf{E} = (\nabla \mathbf{U} + (\nabla \mathbf{U})^T)/2$, $\mathbf{U}$ is the displacement vector, $[\phi] = \phi^\beta - \phi^\alpha$ at the interface, σ is the isotropic interfacial energy, $\mathcal{K}$ is the interfacial curvature reckoned positive for a spherical β particle, and the superscript T denotes transposition. The final boundary condition is the concentration at infinity. We fix the concentration at infinity by requiring that the total volume of the particle phase remain constant,

$$\sum_i \int_{A_i} \nabla C \cdot \mathbf{n} dA' = 0, \quad (3)$$

where A_i is the area of the i th particle–matrix interface.

The velocity at a point on the interface is given by the interfacial mass balance,

$$[C]V = D \nabla C \cdot \mathbf{n}, \quad (4)$$

where V is the local normal interfacial velocity, D is the interdiffusion coefficient in the α phase, and $\mathbf{n}$ is the normal at a point on the interface pointing into the matrix phase. We neglect diffusion in β and shall also set $[C] = [C_i]$, a very good approximation during coarsening.

The stresses in both phases are determined from the equations of elastic equilibrium,

$$\nabla \cdot \mathbf{T} = 0. \quad (5)$$

The boundary conditions used to solve equation (5) are continuity of tractions and displacements at the interface,

$$[\mathbf{T}] \mathbf{n} = 0, \quad (6)$$

$$[\mathbf{U}] = 0, \quad (7)$$

and that the system is traction-free at infinity. The constitutive laws for the stress in the matrix and precipitate are

$$\mathbf{T} = C \bar{\mathbf{E}}, \quad (8)$$

where the elastic strain, $\tilde{\mathbf{E}}$, in the particle is

$$\tilde{\mathbf{E}}^\beta = \mathbf{E}^\beta - \epsilon \mathbf{1}, \quad (9)$$

$\epsilon \mathbf{1}$ is the transformation strain, and in the matrix is

$$\tilde{\mathbf{E}}^\alpha = \mathbf{E}^\alpha, \quad (10)$$

$\mathbf{C}$ is the elastic constant tensor, $\mathbf{1}$ is the unit tensor, and ϵ is the magnitude of the purely dilatational misfit, or transformation, strain.

2.2. System energy

For a system which is evolving according to the above mentioned field equations and boundary conditions, it is possible to identify an energy which must decrease as the system of particles evolve. In the absence of applied tractions, this energy, E_t , is the sum of the total elastic energy of the system, E_e , and the total interfacial energy E_i [32],

$$E_t = E_e + E_i. \quad (11)$$

The total interfacial energy, E_i is simply $\sigma S(t)$, where $S(t)$ is the time dependent interfacial area of all the particles in the system, and t is time.

The total elastic energy of the system can be written as an integral over the interfaces of all the particles [1],

$$E_e = \frac{1}{2} \sum_i \int_{A_i} (\mathbf{U}^\beta - \mathbf{U}^\alpha) \cdot \mathbf{T} \mathbf{n} dA, \quad (12)$$

where $\mathbf{U}^\beta$ and $\mathbf{U}^\alpha$ are the displacements at the interface with respect to the stress-free reference state of each phase. Since the interface is coherent,

$$\mathbf{U}^T = \mathbf{U}^\alpha - \mathbf{U}^\beta, \quad (13)$$

where $\mathbf{U}^T$ is the transformation displacement. Using equation (13) in (12) yields,

$$E_e = -\frac{1}{2} \sum_i \int_{A_i} \mathbf{U}^T \cdot \mathbf{T} \mathbf{n} dA. \quad (14)$$

Thus the total elastic energy of the system can be determined by integrating only over the interfaces of the particles.

For a purely dilatational misfit strain, the transformation displacement and misfit strain can be related as [26],

$$\mathbf{E}^T = \frac{1}{2} (\nabla \mathbf{U}^T + (\nabla \mathbf{U}^T)^T). \quad (15)$$

For a two-dimensional dilatational misfit in the x_1 and x_2 directions the transformation displacement along the x_i direction takes the form [26],

$$\mathbf{U}^T = \epsilon \mathbf{x}. \quad (16)$$

Using equation (16) in (14) yields the total elastic energy of the system via an integration along the interfaces of the misfitting particles.

2.3. Nondimensionalization

The formulation will become more general with the help of nondimensional variables, all denoted in lowercase. The dimensionless forms of the equations are found by using a characteristic strain, ϵ ;

a characteristic elastic constant, C_{44} , where C_{44} is an element of the cubically symmetric elastic constant tensor; a characteristic stress, ϵC_{44} ; and a characteristic length, l , where, for example, in three-dimensions $l = (3V_\beta/4\pi)^{1/3}$, V_β is the volume of one precipitate. Here we choose the characteristic length, l , as $l = (A_\beta/\pi)^{1/2}$, where A_β is the initial area of a particle in two-dimensions, usually the largest particle in the calculation. A dimensionless concentration, c , is defined as

$$c = (C - C_1^*)l/l_c, \quad (17)$$

where l_c is the capillary length in the α phase, $l_c = \sigma B^*$. A characteristic time is defined as

$$\tau = \frac{(C_1^\beta - C_1^*)l^3}{Dl_c}. \quad (18)$$

The dimensionless total energy of the system, e_t is given by, $e_t = E_t/(\sigma l^2)$.

After introducing these dimensionless variables, the total energy of the system becomes

$$e_t = e_e + e_i, \quad (19)$$

where

$$e_e = -\frac{L}{2} \sum_i \int_{A_i} \mathbf{u}^T \cdot \mathbf{t} \mathbf{n} da, \quad (20)$$

$L = \epsilon^2 C_{44} l / \sigma$, and all quantities are dimensionless. The dimensionless parameter L is the ratio of characteristic elastic and interfacial energies. This parameter can be changed within a given alloy system by changing the size of a particle, l . The parameter L also appears in the dimensionless Gibbs-Thompson equation,

$$c^\alpha = L \left\{ \frac{1}{2} [\mathbf{t} \cdot \tilde{\mathbf{e}}] - [\mathbf{t} \cdot \mathbf{e}] \right\} + \kappa, \quad (21)$$

where c^α , $\mathbf{t}$, $\mathbf{e}$, $\tilde{\mathbf{e}}$ and κ are the dimensionless interfacial concentration, stress, total strain, elastic strain and curvature, respectively. Thus L establishes the relative importance of elastic stress compared to the interfacial energy.

The total elastic energy can be decomposed into two energies,

$$e_e = e_e^s + e_e^i, \quad (22)$$

where e_e^s is the elastic self-energy and e_e^i is the elastic interaction energy. The elastic self-energy of a single particle is the total elastic energy of an isolated particle of a given morphology which is embedded in an infinite matrix. The elastic interaction energy of a multiparticle system is, then, the difference between the total elastic energy and the sum of elastic self-energies of each particle. The elastic interaction energy is a measure of the strength of the elastic interaction between particles of a given morphology and spatial arrangement.

3. NUMERICAL METHOD

We solved the above field equations in two-dimensions and in plane-strain with no constraints

on particle morphology. We have employed an explicit time-stepping procedure whereby the elastic field surrounding the particles is first computed and used to determine the interfacial concentrations via the Gibbs–Thomson equation, equation (21). Once the interfacial concentrations are established the diffusion equation is solved and thus the interfacial concentration gradient can be found. By choosing a small time-step, a point on the interface is displaced in the direction normal to the interface using the dimensionless form of equation (4). Since the process must be repeated many times, the numerical algorithm used to determine the stress and concentration field must be quite efficient. For both the diffusion and elastic fields, we only place meshpoints along the interfaces of the particles and thus our resolution of the particle morphologies is quite good. As the details of these algorithms have been presented elsewhere [33], below we only sketch the approach.

The stress field at the interface was determined by evaluating the following integral for the displacement gradient [35],

$$u_{j,k}(\mathbf{x}) = (c_{i11} + c_{i22}) \int_s g_{ij,k}(\mathbf{x}, \mathbf{x}') n'_i ds', \quad (23)$$

where the particle is located in the x_1 – x_2 plane. We employed an effectively analytic form of the Green's function using Stroh's method [36]. To determine the displacement gradient on either side of the interface, we take the limit $\mathbf{x} \rightarrow \mathbf{x}'$ analytically and use an alternating point trapezoidal rule to evaluate the principle value integral. This yields a spectrally accurate numerical method. Since the system is elastically homogeneous and linearly elastic, the elastic field at any point can be found via a simple summation of the elastic fields generated by all particles in the system.

The diffusion field is determined using the same procedure as was used previously in our work on Ostwald ripening in the absence of stress [37, 38]. Here we represent the diffusion field in the matrix using single and double layer potentials distributed over the interfaces of M particles,

$$c(\mathbf{x}) = c_\infty + c_{sl} + c_{dl}, \quad (24)$$

where the single-layer potential is given by

$$c_{sl}(\mathbf{x}) = \sum_{m=1}^M \frac{c_m}{2\pi} \int_s \gamma^{(m)}(\mathbf{x}') \log|\mathbf{x} - \mathbf{x}'| ds', \quad (25)$$

and the double-layer potential is given by

$$c_{dl}(x) = \frac{1}{2\pi} \int_s \mu(\mathbf{x}') \nabla \log(\mathbf{x}, \mathbf{x}') \cdot \mathbf{n}' ds. \quad (26)$$

The constants c_m , c_∞ , the single-layer density $\gamma^{(m)}$ and double-layer density μ are determined by applying the Gibbs–Thomson and mass conservation boundary conditions. Specifically, the single and double-layer potentials are determined by solving singular integral equations. Since the integral equations were solved iteratively, we found that when the elastic interactions between particles were strong, good initial guesses for

the single and double-layer potentials were required to achieve convergence in a reasonable number of iterations. The interface shapes were interpolated using cubic splines.

4. RESULTS

We have used the elastic constant anisotropy ratio of Ni, $A_r = 2.51$, where $A_r = 2C_{44}/(C_{11} - C_{12})$, in all of the calculations. Using the thermophysical data for Ni₃Al particles in a Ni–Al matrix we can calculate the characteristic length and time scales. A Ni–Al alloy with $C_1^f = 0.25$, $C_1^i = 0.13$, $\sigma = 20$ ergs cm^{−2}, yields a capillary length of $l_c = 2 \times 10^{-9}$ cm [39]. For such a Ni–Al alloy, $C_{44} = 1.25 \times 10^{12}$ ergs cm^{−3} and $\epsilon = 0.3\%$, and particle sizes, l , of 0.07, 0.12 and 0.18 μ m correspond to $L = 4, 7$ and 10, respectively. If the evolution process occurs at 900°C, $D = 5 \times 10^{-12}$ cm² s^{−1} and a dimensionless time of $t = 1$ with $L = 4, 7$ and 10 corresponds to dimensional times of approximately 1.2, 6.4 and 18 h, respectively. In all of the figures to follow the sides of the boxes used to display the particle morphologies are located along the elastically soft $\langle 100 \rangle$ directions.

4.1. An isolated particle

In order to provide a basis of comparison when considering the morphological evolution of a multi-particle system, we summarize our past work on the equilibrium shape of an isolated particle with a purely dilatational misfit in an elastically anisotropic system. Figure 1 shows that for $L = 0$, where there is no elastic stress, the equilibrium shape is a circle. This is consistent with the assumption of an isotropic interfacial energy. As the size of the particle increases, L increases and the equilibrium shape assumes a four-fold symmetric morphology, with low interfacial curvature along the $\langle 100 \rangle$ directions and high interfacial curvature along the $\langle 110 \rangle$ directions. At a critical value of L , the four-fold symmetric shapes

Fig. 1. Bifurcation diagram showing the supercritical bifurcation from four-fold symmetric shapes to two-fold shapes at $L = 5.6$, where a_2^* is a parameter which is zero for four-fold symmetric shapes and non-zero for two-fold symmetric shapes [26].

Fig. 2. Temporal evolution of an initially misoriented equilibrium plate-like particle where $L = 10$. The initial rigid body rotation is 10° with respect to the elastically soft direction, $[100]$. (a) $t = 0$; (b) $t = 1$.

become an energy maximum and the energy minimizing shapes are two-fold symmetric shapes located along either $[100]$ or $[010]$. In this case the shape bifurcation occurs at a critical value of $L = 5.6$. As L continues to increase the particles become more plate-like indicating the increasing importance of elastic energy as L increases.

Figure 1 shows that if $L > 5.6$ a two-fold symmetric particle must be located along $\langle 100 \rangle$ for the energy of the system to be minimized. However, if such a two-fold symmetric particle is not located along $\langle 100 \rangle$ then there are a number of evolution pathways by which the particle will attempt to align itself along $\langle 100 \rangle$. For example, Fig. 2 shows the temporal evolution of a two-fold symmetric particle with the equilibrium morphology which is rotated 10° from the $[100]$. In this case the particle maintains approximately the two-fold symmetric morphology and appears to rotate via a dissolution–reprecipitation process to align itself along $[100]$.

Fig. 3. Temporal evolution of an initially misoriented equilibrium plate-like particle where $L = 10$. (a) $t = 0$; (b) $t = 0.0125$; (c) $t = 0.015$; (d) $t = 0.035$; (e) $t = 0.05$; (f) $t = 0.115$.

However, if the rotation of the equilibrium shape from $[100]$ is more extreme, then a different morphological evolution process ensues. Figure 3 shows the morphological development of a particle with equilibrium morphology which is rotated 43° from the $[100]$. In contrast to the evolution process shown in Fig. 2, steps develop along the interfaces which are aligned along the elastically soft $\langle 100 \rangle$ directions and the originally flat ends of the equilibrium shape develop a region of high curvature along $\langle 110 \rangle$. The evolution of the total, interfacial and elastic energies are shown in Fig. 4. The evolution process is driven by the decrease in elastic energy, since the interfacial energy increases a number of times during the calculation. In particular, when the elastic energy is lowered by the development of the steps, the total arc length of the particle, and thus the interfacial energy, increases. However, at later times the interfacial energy tends to reduce the total arc length of the particle. This is attained through reducing the number of steps [see the evolution from Fig. 3(c) to Fig. 3(d)]. After reducing the number of steps the elastic stress orients these steps along the elastically soft directions, see Fig. 3(d) and 3(e). As expected, the total energy of the system decreases monotonically during the entire evolution process. A nearly time independent particle morphology is shown in Fig. 3(f). This three-stepped shape does not have sharp edges and corners due to the non-zero interfacial energy. It is unclear if this shape is an equilibrium shape as the evolution process becomes sufficiently slow after $t = 0.115$ that we cannot follow the evolution of the particle shape any

Fig. 4. Energies as a function of time, t , during the particle evolution shown in Fig. 2. Each $\bigcirc$, from left to right, corresponds to one of the particle morphologies shown in Fig. 2 in alphabetical order. (a) Total energy of the system; (b) total interfacial energy; (c) total elastic energy.

further. While the nearly horizontal slope of the total energy as a function of time curve is consistent with the slow kinetics, it does not imply that the system has reached an energy minimum. It may be an unstable energy extremum such as an energy maximum or saddle point. This competition between the elastic energy and the interfacial energy provides a mechanism to explain the "arrowhead" precipitate morphology found by Ricks *et al.* [40] and the dendritic morphology observed by Yoo and Yoon [41]. The presence of a step-like interfacial morphology such as that shown in Fig. 3(f) is qualitatively consistent with the particle shapes shown in their micrographs. Due to the large variation in curvature along the interface, a large number of meshpoints, 501, was required for this calculation, compared with the typical value used in other cases of 145–181 meshpoints.

4.2. Inverse coarsening in two-particle systems

There is no evidence for inverse coarsening in our two-particle calculations, at least for $L \leq 10$. The only example of transient inverse coarsening we found in a two-particle system is shown in Fig. 5. Inverse coarsening occurs at the beginning of the calculation. However, normal coarsening returns before Fig. 5(b) is reached. As shown in Fig. 6, this rare inverse coarsening, which causes only a 0.01% reduction of the original area of the larger particle, is driven by the decrease in the elastic energy of the system. The initial separation distance of the two particles is larger than the nearly time independent distance mentioned

Fig. 5. Temporal evolution of two initially-aligned equilibrium two-fold symmetric particles where $L = 10$. The initial ratio of the area of the particle on the left to that on the right is 1:0.9. (a) $t = 0$; (b) $t = 0.18$; (c) $t = 0.22$; (d) $t = 1$; (e) $t = 2.12$.

in Ref. [42]. Thus, the particles become longer and thinner in order to decrease the shortest distance between the interfaces of the particles, see Fig. 5(a) and 5(b). As indicated by the minimum in the total elastic energy, Fig. 6(c), the particles then evolve to

Fig. 6. Energies as a function of time, t , during the particle evolution shown in Fig. 5. Each $\bigcirc$, from left to right, corresponds to one of the particle arrangements shown in Fig. 5 in alphabetical order. (a) Total energy of the system; (b) total interfacial energy; (c) total elastic energy; (d) elastic interaction energy.

the most elastically favorable configuration found during the evolution, Fig. 5(c). Since the particles are elongated significantly, this particular configuration gives nearly an extremum in the interfacial energy. The distance between the interior interfaces of the particles decreases until it reaches its lowest value, see Fig. 5(d). This is also where the elastic interaction energy attains its minimum value, see Fig. 6(d). At the same time the particles become thicker in an effort to decrease the total interfacial energy, see Fig. 6(b). Following the particle morphologies shown in Fig. 5(d), normal coarsening ensues and the distance between interior interfaces increases. This increase causes the elastic interaction energy to increase. The total energy of the system, Fig. 6(a), has a nearly zero slope at a time of approximately 1. Nevertheless coarsening continues, thus illustrating that the stability of the system cannot be determined simply from a zero slope of the total energy of the system as a function of time. It is clear from this calculation that changes in particle morphology are driven by a complicated time dependent combination of both the interfacial and elastic energies in the system.

4.3. Inverse coarsening in three-particle systems

4.3.1. Below the bifurcation point. We shall first examine the possibility of inverse coarsening in

Fig. 7. Temporal evolution of three square-like particles which at $t = 0$ have the equilibrium morphology where $L = 4$. (a) $t = 0$; (b) $t = 2.8$; (c) $t = 4.3$.

Fig. 8. Energies as a function of time, t , during the particle evolution shown in Fig. 7. Each $\circ$, from left to right, corresponds to one of the particle arrangements shown in Fig. 7 in alphabetical order. (a) Total energy of the system; (b) total interfacial energy; (c) total elastic energy; (d) elastic interaction energy.

systems in which an isolated particle has a four-fold symmetric equilibrium shape, $L < 5.6$.

Figure 7 shows the coarsening process of three particles with four-fold symmetric shapes located along the elastically soft $\langle 100 \rangle$ directions of the crystal. The two large particles have the same area while the smaller particle has one half the area of either large particle. The evolution of various energies during the calculation is shown in Fig. 8. The area of each particle as a function of time is shown in Fig. 9. Due to the symmetric initial arrangement of the particles, the temporal evolution of the area of both large particles is identical. The area of each particle shown in Fig. 9 is normalized according to the relation, $A_i = a_i/\bar{a} - 1$ where a_i is the area of particle i , and $\bar{a}$ is the average particle area. Thus when $A_i = 0$, the area of this particle equals the average area of the system.

Fig. 9. (a) Area of the particles shown in Fig. 7 as a function of time. (b) Area vs rate of area change. In (b) dA/dt for all the particles is nearly zero at $t = 0$ and increases in magnitude as time proceeds. In both figures the dashed line corresponds to the two initially large particles and the solid line to the initially small particle.

Figure 7 shows that during coarsening the center of mass of the initially small particle moves in the $\langle 110 \rangle$ direction and its area increases monotonically with time. In contrast, the initially large particles stay almost at the same location and their areas decrease monotonically with time. Therefore, inverse coarsening was present during the initial stages of the evolution process, from $t = 0$ to $t = 2.8$, see Fig. 7(a) and 7(b). In particular, in this time interval the total interfacial energy of the system increased by 0.208, see Fig. 8(b). This increase in total interfacial energy was compensated by a decrease in the total elastic energy of an amount, 0.4944, such that total energy of the system decreased monotonically with time. Therefore, consistent with the calculations employing fixed particle morphologies, in this case it is the elastic energy that drives the inverse coarsening process.

Although the total elastic energy decreases considerably during the coarsening process, the total elastic self-energy of the system decreases by only a small amount, 0.0236. Therefore, the decrease in total elastic energy is due mainly to a decrease in the elastic interaction energy. Thus the changes in morphology of the particles are sufficiently small that the elastic self-energy is nearly time invariant and it is the elastic interaction energy which in this case is the driving force for inverse coarsening. However, if the particle morphology were to change significantly, the elastic self energy would change and thus the elastic interaction energy may not play as important a role in the coarsening process. In addition, if the distance between the particles were increased significantly, the magnitude of the elastic interaction would be smaller and thus inverse coarsening would not occur. Finally, note that for $t > 2.8$, where a normal coarsening process is occurring, both the elastic and interfacial energies decrease, and drive the coarsening process. Thus, the elastic interaction energy does not always prevent a normal coarsening process from occurring. This idea is consistent with previous fixed particle morphology calculations [15–17].

The decrease in the elastic interaction energy with time can be understood by considering the elastic interaction energy between selected groups consisting of two particles. The elastic interaction energy between the two particles aligned along the $\langle 110 \rangle$ direction in Fig. 7(a) is positive, while the interaction energy between two particles aligned along the $\langle 100 \rangle$ directions is negative, see Fig. 10. Thus, at a fixed time, the particles aligned along $\langle 110 \rangle$ increase the elastic energy of the system, while the particles aligned along $\langle 100 \rangle$ decrease the elastic energy of the system. The elastic interaction energy is also proportional to the area of the particle. Therefore when the smaller particle grows the elastic energy of the system decreases, as it is aligned along $\langle 100 \rangle$ with respect to the large particles. Conversely, as the larger particles are aligned along $\langle 110 \rangle$ the elastic energy of the system would increase if they were to grow. Thus, the small particle

Fig. 10. Elastic interaction energies between two of the particles of Fig. 7, in the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. Each $\bigcirc$ corresponds to one of the particle arrangements shown in Fig. 7 in alphabetical order.

grows at the expense of the two larger particles and inverse coarsening takes place. These results can also be explained on the basis of interactive configurational forces [42].

In an effort to examine the stability of particle doublets in elastically anisotropic systems, we examined the evolution of three particles with the same shapes and areas as those in Fig. 7 but with a different arrangement as shown in Fig. 11. Here a particle doublet aligned along $[100]$ is created by bringing the initially-smaller particle closer to one of the initially-larger particles. The purpose of this calculation was to determine whether the small particle would shrink with respect to the closer large particle, or if this small

Fig. 11. Temporal evolution of three particles with the same shapes as those in Fig. 7 but in different relative orientation, L is still 4. (a) $t = 0$; (b) $t = 1.4$; (c) $t = 1.7$; (d) $t = 2.2$; (e) $t = 2.5$; (f) $t = 2.6$.

Fig. 12. Energies as a function of time, t , during the particle evolution shown in Fig. 11. Each $\circ$, from left to right, corresponds to one of the particle arrangements shown in Fig. 11 in alphabetical order. (a) Total energy of the system; (b) total interfacial energy; (c) total elastic energy; (d) elastic interaction energy.

particle would grow at the expense of the other larger particle located farther away from this small particle.

The temporal evolution of the energies, Fig. 12, show similar trends as those illustrated in Fig. 8, except that the interfacial energy reaches its maximum value earlier than in the former case. As the interfacial energy increases initially, there is clearly an inverse coarsening process occurring in this system. More importantly, as illustrated in Fig. 13, the small particle does not shrink away initially, as it would if the large particle in the upper right corner of Fig. 11 was not present. The shrinking initially-larger particle evolves in a way similar to the corresponding one in Fig. 7, but with a faster coarsening rate (compare

Fig. 13. (a) Area of the particles shown in Fig. 11 as a function of time. (b) Area vs rate of area change. At $t = 0$ dA/dt is nearly zero for all three particles, and for two of the particles dA/dt increases in magnitude as time proceeds. In both figures the dashed line corresponds to the two initially large particles and the solid line to the initially small particle.

the magnitude of dA/dt in Figs 9 and 13). The mass flows from this shrinking larger particle to the other two particles in the system. It is this influx of mass to the two-particle subsystem that causes the initially smaller particle to grow. As soon as the area of the growing larger particle is slightly larger than the total area of the other two particles and the initially small particle attains its maximum area, a time just before Fig. 11(c), the smaller particle begins to shrink at a very slow rate and the largest particle in this system begins to absorb all the mass flowing from the other two particles.

Unlike Fig. 7, the morphology of the particles in this case changes dramatically, especially that of the

Fig. 14. Temporal evolution of three aligned unequal-sized particles where $L = 10$. (a) $t = 0$; (b) $t = 0.14$; (c) $t = 0.18$; (d) $t = 0.53$.

Fig. 15. Dimensionless energies corresponding to the evolution shown in Fig. 14. Each $\circ$ corresponds to one particle morphology of Fig. 14 in alphabetical order. (a) Total energy of the system; (b) interfacial energy; (c) total elastic energy; and (d) elastic interaction energy.

Fig. 16. (a) Area of the particles shown in Fig. 14 as a function of time. (b) Area vs rate of area change. In (b) dA/dt for all the particles is nearly zero and increases in magnitude as time proceeds. In both figures the dashed line corresponds to the two initially large particles and the solid line to the initially small particle.

growing particles. Thus, in this case the elastic energy decreases not only due to a change in the elastic interaction energy, but also due to a change in the elastic self-energy. This change in the elastic self-energy is a result of the change in the morphology of the particles. This change in particle morphology is caused by the strong diffusional and elastic interaction between the two particles aligned in the [100] direction.

4.3.2. Above the bifurcation point. Here we are interested in the mechanisms underlying the coarsen-

ing process of a group of two-fold symmetric particles located along the elastically soft direction of the crystal. The value of L exceeds the bifurcation point for the equilibrium shape of an isolated particle; the equilibrium shape of a particle is two-fold symmetric. Such arrangements are found in many systems [1]. The temporal evolution of three aligned plate-like particles with an initial area ratio of 1:0.7:1 is shown in Fig. 14. The evolution of the various energies is shown in Fig. 15, and the evolution of the areas of

Fig. 17. Total energy surface for an isolated two-circular-particle system. E along $R = 0$, $D = 0.047$, $D = 0.447$ and $D = 2.447$ are denoted as darker lines, where E is the total energy, and $R = R_a$.

the particles is shown in Fig. 16. In this case, inverse coarsening occurs from the beginning of the calculation. The interfacial energy increases at early times due to the elongation in the particle morphology along $\langle 100 \rangle$ and the reduction in the distances between the particle interfaces, Fig. 14(b). The elastic energy continues to drive this inverse coarsening process by increasing the width of the particles until reaching its minimum value at $t = 0.18$, Fig. 14(c). After this time the elastic energy in the system increases due to the change in particle morphology from plate-like shapes to more square-like shapes. This change increases the elastic self-energy of the particles and decreases the total interfacial energy of the system. However, the smaller particle is still growing at the expense of the two larger particles, see Fig. 16(a), and thus the decrease in interfacial energy and elastic interaction energy is driving the inverse coarsening process, Fig. 15(b) and (c). By $t = 0.53$ the initially smaller particle is now the largest particle in the system, and thus a normal coarsening process is underway.

5. DISCUSSION

The classical description of the effects of elastic stress on coarsening has been in the context of energetic calculations in systems consisting of particles of a fixed morphology. To compare our results with this classical approach, we have examined the total energy of two circular particles in an elastically anisotropic system. We follow closely the procedure developed by Johnson [9] and used extensively by Miyazaki and co-workers [12–14]. The total energy of the two-particle system is defined using equation (19),

$$e_t = e_c^s + e_c^i + e_i, \quad (27)$$

where: $e_t = e_t(R_a, D, L)$, $e_i = e_i(R_a)$, $e_c^s = e_c^s(R_a)$, $e_c^i = e_c^i(R_a, D)$, $R_a = (a_1 - a_2)/(a_1 + a_2)$, D is the shortest distance between the interfaces of the particles, and a_i is the area of particle i . The total energies for various values of L are shown in Fig. 17, where R_a ranges from -1 to $+1$, D ranges from 0.047 to 2.447 , and the total area of both particles has been fixed at 2π . The energy was calculated numerically using the above mentioned procedure. Following Johnson's work, the possibility of inverse coarsening can be viewed as bifurcation in the extrema of the energy of this two-particle system. In the absence of elastic energy, two particles of equal size, $R_a = 0$, are always an energy maximum. However, if inverse coarsening is a possibility and, in particular, if the system is stable with respect to coarsening $R_a = 0$ must be an energy minimum. Thus, the stability of the system with respect to coarsening can be determined by examining the sign of $\partial^2 e_t / \partial R_a^2$ evaluated at $R_a = 0$ as a function of D and L .

For $L < 5.881$ $\partial^2 e_t / \partial R_a^2 < 0$ at $R_a = 0$, for any D , indicating that two particles of equal size are energy maxima and the system is unstable with respect to

coarsening. However, it is also evident from Fig. 17 that $\partial^2 e_t / \partial D^2 > 0$ at $R_a = 0$ over a range of distances. The location of the relative energy minimum is $(R_a, D, L) = (0, 0.447, 5.881)$ indicating that two circular particles of the same size will attract one another and there will be an equilibrium separation distance between the particle interfaces of magnitude 0.447 .

However, for $L = 5.881$ and at a distance at which the elastic interaction energy is a maximum, $D = 0.447$, $\partial^2 e_t / \partial R_a^2 = 0$. Thus, for $L > 5.881$ two particles of equal size can be stable with respect to coarsening over a certain range of interparticle separation. The relative energy minimum becomes broader and deeper with increasing L indicating that the propensity of the system to undergo inverse coarsening increases with increasing L . Thus, if the initial distance between the particles and the radius ratio is such that the second derivatives of the energy of the system are positive, inverse coarsening will occur and the system will evolve to two equal-sized particles separated by a certain equilibrium distance. Finally, two particles of equal size in many cases are only a relative energy minimum, thus they are metastable with respect to the formation of one large particle.

To compare these results with our time dependent calculations, where we do not constrain the morphology of the particles to be circular, we considered the stability of a two particle system with respect to small changes in the area of one particle. We first examined the stability of two particles with an initially four-fold symmetric equilibrium shape, where L is below the bifurcation point of 5.6 , located at the equilibrium separation distance $[42]$. Here we decreased the area of one particle by making the area ratio $1:0.96$ or $R_a = 0.02$. We found that such particle doublets were always unstable with respect to coarsening. We performed similar calculations above the bifurcation point, where the equilibrium shape of an isolated particle is two-fold symmetric, and found identical results: for $L \leq 10$ particle doublets are unstable with respect to coarsening. While small amounts of inverse coarsening were observed, see Fig. 5(a), two particles with equal areas were never stable with respect to coarsening. Therefore, we conclude that the energetic calculations of the stability of two circular particles with respect to coarsening yielded qualitatively incorrect results. The reason for this error lies in the constraint that the morphology of the particles remain circular. When this constraint is relaxed, the number of degrees of freedom in the system increases beyond two, R_a and D , and thus the system is free to explore other morphological evolution paths, which in this case decrease the energy of the system. This is consistent with Onuki's assertion that changes in the shapes of particles alter dramatically the elastic interaction energy between the particles [18].

In contrast to previous results, primarily those based upon energetic calculations with particles of

fixed morphology, during the morphological evolution of the three aligned two-fold symmetric particles shown in Fig. 14, inverse coarsening was observed even though the total elastic energy *increased* and the total interfacial energy *decreased*. The elastic interaction energy, however, decreases during the entire calculation. Thus, in this case the growth of the smaller particle at the expense of the larger particles, inverse coarsening, was driven by a decrease in the interfacial and elastic interaction energy. The increase in elastic energy and decrease in interfacial energy from $t = 0.18$ to $t = 0.53$ are due to changes in the aspect ratios and detailed morphology of the particles during the evolution process. For example, by $t = 0.53$, Fig. 14(d), the small plate-like particle is thicker than the other two initially larger particles and the thickness of the initially larger particles varies with position along $\langle 100 \rangle$. The result provides an illustration of the complex morphological evolution which is possible in stressed systems when the morphology of the particles is not fixed. Since two-dimensional, plane strain, conditions are assumed, the particle size in the third direction is assumed to be much larger than in the other two directions. Thus, the particle cannot change its size or shape in the third direction. While this may overly restrict the morphological development of a particle in some cases, it is very difficult to determine the effects of this constraint without performing full three-dimensional calculations.

Inverse coarsening was almost never observed in the two-particle calculations. It was very easy, however, to arrange three particles such that inverse coarsening will take place. Thus, we expect that localized inverse coarsening in multiparticle systems is quite common; the calculations of Wang *et al.* support this conclusion [21]. However, in all of the three-particle calculations performed, the system never coarsened to a state with more than one particle that was stable with respect to coarsening. Thus, although inverse coarsening occurred during a portion of the morphological evolution process, the elastic stress was never sufficient to stabilize an array of particles against coarsening.

During coarsening it is not unusual to find plate-like particles aligned along the elastically soft directions of a crystal. An immediate question suggested by this particle arrangement is the mechanism by which these aligned particles coarsen. It has been shown by a number of authors [21, 27, 29], that these particles can coarsen via a coalescence process, i.e. the physical contact of particle interfaces. Our calculations show that such coalescence is not necessary for the coarsening process to proceed, see Fig. 14. In this case coarsening occurs by mass flow across the small regions of matrix which separate the particles. By focusing on the motion of the thin region of the matrix, this process can be viewed as a migration of a thin film of matrix along a certain direction. The end result of this migration is one large two-fold

shaped particle which has the energy minimizing shape.

We found that a doublet consisting of a small and large particle can grow at the expense of another large particle located at some distance from that doublet. This result is an illustration of a mechanism for particle alignment along the elastically soft directions of a crystal. In this case, the smaller particle did not shrink in size due to the negative elastic interaction energy with the neighboring large particle. This shows that a selective coarsening process, such as that suggested by Ardell and Nicholson [1], can lead to particle alignment in an elastically anisotropic system.

6. CONCLUSIONS

On the basis of our calculations of the morphological evolution of particles with a dilatational misfit in an elastically anisotropic system we find that:

- During coarsening in elastically stressed systems neither the total interfacial energy nor the total elastic energy must decrease monotonically with time. For systems such as those considered herein, only the sum of these two energies must decrease with time.
- When the morphology of two particles is fixed as circles, two particles of the same radius can be stable with respect to coarsening. However, if changes in particle morphology are allowed to occur which are consistent with mass diffusion and the conditions for local interfacial equilibrium, two-particle systems were never observed to be stable with respect to coarsening.
- Inverse coarsening is more easily observable in multiparticle systems, but stabilization of a multiparticle system with respect to coarsening was never observed.
- Due to the complex morphological changes induced by interparticle elastic interactions, inverse coarsening can be accompanied by a *decrease* in the interfacial energy of the system, as would be the case in a classical coarsening process.
- The growth of a group of particles aligned along an elastically soft direction of the crystal at the expense of an isolated large particle is one mechanism by which the experimentally observed raft-like particle arrangements can form.
- Two-fold symmetric, plate-like, particles aligned along the elastically soft direction of the crystal can coarsen by mass flow through the thin interparticle regions of matrix.

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