COARSENING IN MULTICOMPONENT MULTIPHASE SYSTEMS

A Final Report for
DOE Grant DE-FG03-96ER45556

by

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October 22, 1999

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The following report summarizes the significant results obtained from Department of Energy contract no. DE-FG03-96ER45556. The project entitled "Coarsening in Multicomponent Multiphase Systems" has resulted in four publications in refereed journals (two in preparation) and three presentations at professional scientific conferences (one invited). In addition, the research conducted was the topic of a PhD dissertation by graduate student Will Holmes, now an assistant professor of physics at Taylor University in Upland, IN.

The goal of the project was to extend the theory of particle coarsening, which is well established for binary systems, to the case of multicomponent and multiphase alloys. The theoretical approach involved three stages: 1) a mean field description based on the Lifshitz-Slyozov-Wagner (LSW) [1,2] formulation (recently published in *Acta Mater*. [3]), 2) an analytical description of coarsening valid at small volume fractions where the Marqusee and Ross [4] model was employed and 3) a numerical simulation of three phase coarsening where the boundary integral method of Akaiwa and Voorhees [5] was implemented.

The main result of the mean field analysis can be stated as follows. The growth rate of a particle from a particular phase in a multiphase system is precisely the same as that derived for a single phase, multicomponent system. Also, it was found that the scaled particle size distribution for each phase in the system has exactly the same form as that originally derived by LSW. Since it neglects particle interactions, the mean field theory is clearly unrealistic and as such the formulation of coarsening in low volume fraction multiphase systems was undertaken.

Marqusee and Ross used a multiple scattering technique to examine the effect of nonzero volume fraction on the coarsening behavior in binary systems. Results for the coarsening rate constant, the particle number density and the scaled particle size distribution were all derived in the limit of long aging time. The most significant result of our research was the fact that the problem of coarsening in a multiphase multicomponent system can be mapped onto the binary problem in a very straightforward and transparent way. In particluar it was discovered that the coarsening behavior of a given phase within the multiphase system can be found from the binary Marqusee and Ross result by simply replacing its actual volume fraction by a so-called "effective volume fraction". Consider a system with two low volume fraction phases, β and γ ripening in a matrix α. The effective volume fraction of the β phase is given by:

$$\phi^{\beta}_{eff} = \phi^{\beta}\left(1+\Gamma_{\gamma\beta}\frac{\phi^{\gamma}}{\phi^{\beta}}\right) \qquad 1$$

where ϕ^{η} ($\eta=\beta,\gamma$) is the actual volume fraction and $\Gamma_{\gamma\beta}$ is the important "cross phase coupling constant" which is a measure of what effect the second coarsening phase (in this case γ) has on the coarsening behavior of the β species. $\Gamma_{\gamma\beta}$ is given by:

$$\Gamma_{\gamma\beta} = \frac{D_2 \Delta c_1^{\alpha\beta} \Delta c_1^{\alpha\gamma} + D_1 \Delta c_2^{\alpha\beta} \Delta c_2^{\alpha\gamma}}{D_2 \left(\Delta c_1^{\alpha\beta}\right)^2 + D_1 \left(\Delta c_2^{\alpha\beta}\right)^2} \tag{2}$$

Here D_1 and D_2 are the diffusion coefficients of species 1 and 2 in the matrix phase (we have assumed a diagonal diffusivity matrix). Also, the quantities $\Delta c_i^{\alpha\eta}$ $(i = 1,2; \eta = \beta, \gamma)$ denoted the equilibrium concentration difference between species i in the matrix phase and the precipitate phase η. The effective volume fraction description avoids the complicated multiple scattering derivation for multiphase systems and circumvents numerical modeling in the low volume fraction limit. Equations 1 and 2 demonstrate very simply how the coarsening in a three phase system depends on the volume fraction of both phases, the relative diffusivities of the two solute species and the topology of the equilibrium three phase triangle within the isothermal section.

To illustrate the ease with which the effective volume fraction method can be utilized to decipher the complex problem of multiphase coarsening, consider the isothermal section shown in fig. 1. Notice that the three phase triangle has sides which lie parallel to the Gibbs triangle, this means that eg. the β phase requires species 1 from the matrix in order to grow, but, since the composition of species 2 is the same as the α matrix, the β particles do not absorb concentration 2. An analogous argument can be used to show that the γ precipitates grow independently of species 1. Intuitively one would expect that in this case the coarsening rate of β does not depend on the presence of the γ phase and vice versa. Indeed the effective volume fraction idea reproduces this result. Since $\Delta c_2^{\alpha\beta} = 0$ and $\Delta c_1^{\alpha\gamma} = 0$, the effective volume fraction reduces to the actual volume.

A number of important results were obtained from the third focus area of the project, ie. numerical simulations. The simulations were performed using a boundary element, multipole expansion formulation and each run typically started with 20,000 total particles. Simulations at low volume fractions of each phase confirmed the effective volume fraction prediction of coarsening behavior, the average growth rate obtained from the simlutaions agreed to within a few percent with the predictions of eqs. 1 and 2. At higher volume fractions the simulations provided a means of studying spatial correlations between particles and it was shown that again the cross phase coupling constant plays a key role. For example, two simulations were performed with equal actual volume fractions of β and γ, but with different effective volume fractions. The simulation with the larger $\Gamma_{\gamma\beta}$ showed a very different β–γ pair correlation function as evidenced by a much larger depletion zone around a given particle. The results agree with the intuitive picture of multiphase coarsening developed above, a larger cross phase coupling constant implies a stronger degree of β–γ interaction.

A third significant result concerns the structure functions from the ternary, three phase systems. The structure function is the Fourier transform of the auto-correlation of the concentration and depends on the size and spatial distribution of all the particles. In a

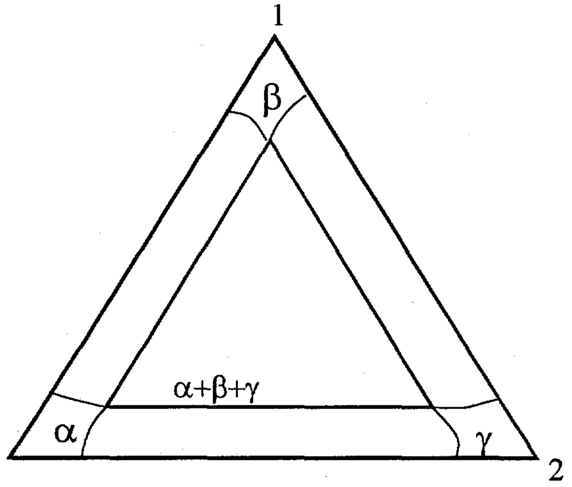

Fig. 1. Isothermal section of a ternary three phase system. For this system, coarsening of the β(γ) depends only on the volume fraction of β(γ).

small angle x-ray or neutron experiment. Typically the scattered intensity exhibits a peak at small wavenumber and the peak height increases and the peak position moves toward the origin as coarsening proceeds. It has long been known that the structure function in a binary system obeys dynamic scaling, that is if the structure functions for various aging times are replotted on a scale of k/k_m where k_m is the peak position, then all the curves collapse to a single time independent function. The scaling property demonstrates that the evolving system is self-similar, the microstructure at any two given aging times differ by only a scale factor. In the ternary case three rather than one structure function needs to be considered and our simulations have shown for the first time the existence of scaling in multiphase systems.

Perhaps the most interesting result of the numerical simulations, however, concerns the notion of morphological instability. It is known that binary systems remain stable during coarsening in the sense that a more or less homogeneous distribution of particles is observed at all aging times. For the three phase case, we have shown both analytically and by simulations that there are special cases in which the ripening process is unstable. Specifically, for instances in which the cross phase coupling constant is negative, coarsening is characterized by spatial regions which contain a high density of very large particles separated by regions of very low particle density. The behavior is reminisent of the Liesegang phenomenon in chemically reacting systems. The existence of morphological instabilities provides a dramatic illustration of the very different behavior possible due to the extra degree of freedom found in a multiphase system.

References

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