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Self-similar coarsening: A test of theory

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ABSTRACT

Theoretical description of coarsening is of central importance to describing the kinetics of phase transformations in a wide range of materials. Through experiments on the International Space Station (ISS), the dynamics of coarsening was measured in a system that satisfies all assumptions of theory, in which the materials properties needed to compare experiment and theory are known, and has a rapid coarsening rate. The observed exponents for the temporal power laws match those predicted by theory. We find that the amplitudes of the power laws are slightly higher than predicted due to the presence of slow particle motion resulting from nonzero gravity present on the ISS. The measured particle size distributions are in agreement with those predicted by simulations. We conclude that interfacial energy driven coarsening is well described by theory and that simulations of coarsening can be used as a reliable tool for computational materials design.

1. Introduction

Ostwald ripening, or coarsening, is a diffusion driven, competitive growth process through which the total energy of a system is reduced via the reduction of interfacial area. It is a common process that takes place in many multi-phase systems and is of particular importance during the late-stage processing of alloys. In a simple two-phase system, coarsening is characterized by the growth of large domains of a phase at the expense of smaller ones. Throughout the process, the total number of domains decreases while the volume fraction of the phase remains roughly constant. In this manner, a system consisting of many, small precipitates, when left to coarsen indefinitely, will eventually consist of only a few, large precipitates.

The microstructure of a system is characterized by the size, shape and distribution of these features and as such, can be largely determined by the coarsening process. Since the microstructure of a material dictates the macroscopic properties of that material, such as strength or toughness, the manner and rate at which a system coarsens will have a significant impact on the ultimate characteristics of the material. A thorough understanding of the underlying mechanisms of the coarsening process will allow it to be used as a tool to tailor materials to possess specific, desirable qualities. Due to the ubiquity of the coarsening process, this tool would be applied to a wide range of potential systems. Ultimately, a robust theory of coarsening will provide the basis for more powerful and efficient techniques in the field of computational materials design.

There have been numerous attempts to develop a theory for describing a coarsening system, beginning with the seminal work of Lifshitz, Slyozov and Wagner [1,2]. In analyzing a system of infinitely separated solid, spherical particles in a liquid matrix, they came to a number of important conclusions, collectively known as LSW theory. The theory states that in the infinite time limit, $t \to \infty$, the system reaches a steady state in which there exists a critical particle radius, above which particles will grow, and a maximum particle size radius to the average particle radius. The system is self-similar, that is the particle size distribution (PSD), when scaled to the average particle radius will be independent with time. Additionally, in the case of diffusion limited coarsening, the average particle size will evolve with time as

$$\langle R(t)\rangle^3 - \langle R(0)\rangle^3 = K_R^{LSW} t \tag{1.1}$$

where $\langle R(t)\rangle$ is the average particle radius at a given time t, $\langle R\rangle(0)$ is the initial average particle radius, and K_R^{LSW} is a rate constant depends on the thermophysical parameters of the system. Similarly, the average particle number density evolves as

$$N_V(t) = K_N^{LSW} t^{-1} \tag{1.2}$$

where N_V is the particle number density and K_N^{LSW} is the rate constant governing the law.

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Though a significant foundation in the study of coarsening kinetics, the inherently unrealistic assumption in LSW theory of infinitely separated particles fails to fully describe the underlying behavior of the coarsening process. As the volume fraction increases, the form of the temporal dependence of R and N_V will be the same as the LSW theory in the dilute limit, but the rate constants $K_{R,N}$ will depend on the volume fraction. Subsequent studies have aimed to expand this treatment to non-zero volume fraction systems [3–10], including simulations utilizing both phase-field simulations [11–13] and solutions to the multi-particle diffusion problem [14–17], which, in the case of zero volume fraction, reduce to the LSW limit. However, there still exists large disagreement on the dependence of the rate constants and the form of the PSDs on the solid volume fraction and even claims that the theory is incorrect [18] or missing important physics [19].

Despite the pervasiveness of the coarsening process and the large number of theories, there is a dearth of parameter-free experimental tests of the theories. This is primarily because there are very few systems in which the materials parameters needed to compare theory and experiment are known, and can be coarsened for sufficient time to reach the self-similar state that is predicted by theory. Wang and Glicksman [17] performed an experimental comparison that showed good agreement of the PSDs in the self-similar state but poor agreement with the rate constants due to the interfacial energy and diffusion coefficients of the system being unknown. Solid particles suspended in liquids are ideal systems in which to study coarsening. However, Earth's gravity and the difference in density between the solid and liquid phases, results in sedimentation and, therefore, non-uniformly distributed particles [20]. The International Space Station (ISS) and the microgravity environment it provides, thus gives an unprecedented opportunity to test the aforementioned theoretical predictions. Early experiments were either restricted to very short coarsening times [20–22], where the system had not yet reached steady state, or employed very high volume fractions for which the theoretical assumptions used in the nonzero volume fraction theories no longer apply [23].

2. Experimental methods

In order to directly compare the multitude of coarsening theories to experimental results with no adjustable parameters, a candidate system needs to have a certain number of ideal qualities, including:

- interfacial energies such that the particles (i.e. the coarsening phase) are or are nearly spherical
- materials with well characterized diffusivities and interfacial energies allowing for a quantitative comparison
- a stress-free matrix phase, without which the morphology of the particles and kinetics of the process can be severely altered
- a system that coarsens at a sufficient rate such that a significant change in the average particle size can be observed in a reasonable amount of time, accessing the self-similar state and yet making the experiment feasible.

With these desired characteristics in mind, two-phase solid liquid systems are singled out as a good potential system for the investigation of the coarsening process.

A tin rich lead–tin (PbSn) alloy is an ideal candidate for coarsening experiments. The interfacial energy between the solid Sn-rich particles and the eutectic liquid ensures spherical particles, and the materials parameters have been well characterized in grain boundary grooving experiments performed by Hardy et al. [24]. The system forms a eutectic at $\sim$ 183 °C which satisfies the stress free matrix condition in that the system will consist of solid Sn-rich particles suspended in a PbSn eutectic liquid, with the added benefit of the eutectic temperature being relatively low and easy to achieve in a laboratory setting. The coarsening is limited by diffusion through the matrix rather than evaporation/condensation at the particle surface and, over the course of a coarsening experiment (up to 48 h), the average particle size will increase four to fivefold.

PbSn alloys of varying solid Sn volume fractions are produced following the process outlined by Hardy and Voorhees [25]. 99.9999% purity tin shot and lead ingots are measured and cast into a chilled steel mold. The resulting ingots are severely cold worked via swaging before being machined into cylindrical samples approximately 1 cm in diameter and 6 mm in height, with some additional fine machining to ensure that each sample is appropriately sized for the holder in the furnace in which it is to be aged. The samples are then placed within their respective furnaces, where they remain throughout the experiment.

To counteract the effects of sedimentation that arise due to the difference in density between Pb and Sn, the samples were processed aboard the ISS. As part of the third iteration of the Coarsening in Solid Liquid Mixtures project (CSLM-2R) the furnaces containing the samples were transported to the ISS, where they were loaded into the microgravity glovebox. After installation, the furnaces, each containing a range of solid volume fraction samples, were run for a range of coarsening times. The furnaces were heated to a coarsening temperature of 185°C, just above the PbSn eutectic temperature. The eutectic liquid penetrates the grain boundaries between the tin, creating a dispersion of Sn crystals that rapidly become spherical. After being held at this temperature for the predetermined amount of time, the samples are quenched with water. They remain in the furnaces until they are brought back to earth, where they are placed at −80°C until ready for characterization and analysis. The low temperature storage is necessary to ensure that the eutectic does not coarsen at room temperature, which is possible due to its low melting temperature, since a coarser eutectic leads to poor contrast between phases under optical imaging.

The microstructural analysis of the PbSn samples was performed using an automated mechanical serial sectioning method designed by Alkemper and Voorhees [26,13] utilizing a custom modified micro miller fitted with an optical microscope. With a repeatable, adjustable section thickness (down to $\sim$ 2 μm) and an external alignment reference via a Linear Variable Differential Transformer (LVDT), up to $\sim$ 20 sections per hour can be obtained, where a typical data set will consist of 400–500 two-dimensional (2D) sections.

Before the three-dimensional (3D) volume can be reconstructed from the acquired data, each optical image must be registered, cleaned and segmented into binary images, with each pixel in the image identified as either solid Sn or eutectic. This is achieved through a combination of automated algorithms and manual cleaning. The bulk of image registration is performed using the data from the LVDT, which records translational displacement of the sample in between sections. This alignment is fine tuned using a cross correlation algorithm, typically on the order of a few pixels. Surface artifacts, such as scratches, drying residue or uneven etching are removed using median filtering. To segment the images, the Expectation Maximization/Maximization of Posterior Marginals (EM/MPM) method is used [27]. EM/MPM is a step beyond simple thresholding that combines global information from the image histogram with local information to find the most probable segmentation. Additional fine tuning of the segmentation is achieved using median filters, size filters and some minimal manual cleaning before reconstruction.