CHAPTER 4.2

Coarsening in a Spinodally Decomposing System: TiO₂–SnO₂

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1. Introduction

Solid solutions can decompose (i.e. exsolve) via two distinct mechanisms—spinodal decomposition or nucleation and growth—and there are several easily defined differences between them, particularly during the early stages of decomposition (Cahn, 1968). Of these differences, probably the most important is that there is no nucleation barrier for spinodal decomposition, the kinetics of decomposition being controlled entirely by diffusion; in contrast, the nucleation barrier in conventional nucleation and growth theories gives rise to the well-known idea of a critical nucleus. During spinodal decomposition, therefore, spontaneous composition fluctuations of various wave numbers form, and those with maximum amplification factors dominate the microstructural evolution. When the amplitude of the composition fluctuations approaches that given by the equilibrium phase diagram, a late stage of decomposition has been reached and further microstructural changes represent a coarsening phenomenon. At this stage of decomposition, there is little conceptual difference in the coarsening behavior between systems that initially decompose spinodally and those that decompose by nucleation and growth, in that coarsening in both is controlled by the diffusion kinetics.

The usual kinetic equation for describing coarsening is

\[ \lambda^m \propto K t \]

where \( \lambda \) represents the size of the average precipitate particle at time \( t \) and \( K \) and \( m \) are constants. In the present work, it will be shown that this equation adequately describes coarsening in TiO₂–SnO₂ “alloys” with \( m = 3 \). Before describing our results, however, it will be useful to review briefly the relevant literature on coarsening in other systems.

Ardell and Nicholson (1966) were among the first to study coarsening using electron microscopy. They determined the growth kinetics of precipitates in a Ni-Al alloy which had formed via a nucleation and growth mechanism, and showed that the kinetic equation accurately described their data at temperatures between 625 and 775 °C with \( m = 3 \), in agreement with the coarsening theories of Lifshitz and Slyozov (1961) and Wagner (1961). In systems that decompose spinodally, however, the earliest study was apparently that performed by Hillert et al. (1961) on a Cu-Ni-Fe alloy; they estimated the magnitude of composition
Fig. 1. (a) Single-phase equimolar TiO$_2$–SnO$_2$ alloy annealed at 1580 °C and quenched into water. (b) Equimolar TiO$_2$–SnO$_2$ specimen annealed at 1500 °C and air-quenched. The background structure is evidence that some decomposition has occurred. (c) Sample of Fig. 2 after annealing for 5 min at 1000 °C; (d) after annealing for 60 min at 1000 °C; (e) after annealing for 15 h at 1000 °C. All micrographs are same magnification.