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Some remarks about the kinetics of the competitive growth in multicomponent systems

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ABSTRACT

Kinetics of the competitive growth of k-phases during the diffusive decomposition is commented on multicomponent solid solutions. It analyzes how the common component among phases controls their survival. Equations that determine the kinetic behavior of a multicomponent system with k-phases, in the last stages of the diffusive decomposition, are discussed taking into account the common component (or controller component). The parameters that determine which of these phases will survive during the competitive process are deduced.

1. Introduction

The classical theory of phase coarsening in binary systems was firstly developed by Lifshitz and Slyozov (LS) [1], and later by Wagner (W) [2]. The LSW (Lifshitz-Slyozov-Wagner) theory predicts that, for asymptotically long aging times, the cube of the average particle radius increases linearly with time and that the supersaturation of solute in the matrix decays as $t^{-1/3}$. Phase coarsening in binary systems has been studied in considerable depth by many researchers in the last decades. Some of these classical formulations have been recently reviewed and discussed [3].

Since most materials of commercial interest are not binaries, it is of interest to extend the analysis of coarsening kinetics to ternary, multicomponent and multiphase systems. One of the first studies on coarsening in ternary systems was carried out by Bhattacharyya and Russell [4]. These authors assumed that the coarsening rate constant was controlled by that species in solution which exhibited the smallest product of diffusion coefficient times equilibrium concentration. Björklund et al. [5] and Slezov and Sagalovich [6-8] considered the problem of phase coarsening in multicomponent systems, restricted to dilute solutions. Kuehmann and Voorhees [9] and Umantsev and Olson [10] derived a coarsening rate for the case of a single precipitate phase of arbitrary composition in a non-dilute matrix phase, but did not consider the effects of interfacial curvature on the precipitate composition in their multicomponent phase coarsening. Morral and Purdy [11-12] developed an initial theory for phase coarsening in *n*-component alloys. However, they predicted only the temporal evolution of the average particle radius, and that the solution thermodynamics in no way affects the coarsening kinetics. Philippe et al. [13] studied Ostwald ripening in multicomponent alloys and focused on the thermodynamic effect of the multicomponent. All these works mentioned above considered only the thermodynamic effect, ignoring the kinetic effect from the nonzero volume fraction. In spite of the research published on this subject, even the theory and simulations for phase coarsening in multicomponent systems are rare [14].

Phase competition in late stages of the diffusive decomposition in multicomponent systems has been scarcely treaty in the

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literature. One of these papers [15], applying the formalism referred in Refs. [6-8], showed that a competition is possible between phases having a common component. The final result of this competition showed that only one of these phases survives. In this paper [15], the conditions for existence of phases are determined. In this sense, when the common component of the different phases is almost completely absorbed, while the rest of component remain in solution, a competition then begins between the phases for the insufficient common component. At the end of the diffusive competition, only one of the phases survives manifesting a universal size distribution function independent of the initial distributions.

The above analyzes [6-8,15] are not detailed on the parameters that could determine the kinetics of the phases survival during the last stages of the diffusive decomposition. The present approach, following the reasoning of [6-15], obtains a parameter that could measure the “thermodynamic disadvantages” of each phase during the competitive growth. Finally, it is proposed a sequence in which k-1 stoichiometric phases in a multicomponent system will be disappearing during the competition.

2. Basic equation system and discussion

According to [8], it is considered a n-component solid solution with a small volumetric fraction of precipitated particles corresponding to k-phases. Besides, it is assumed that as the ratio of the average size of precipitates ($\bar{r}$) to the average distance ($\bar{l}$) between them is small ($\bar{r} \ll \bar{l}$), a direct interaction among precipitates can be discarded during the diffusive competition. Since the precipitate growth rate depends on their sizes and the phase particularities, the above condition limits this approach to systems where the growth rates of all stoichiometric phases are in the same order.

Then, the basic equations that allows to characterize the above system have k-continuity equations in the size space (1) and n laws of the matter conservation of the components [6-8] (2):

$$\frac{\partial f^s}{\partial t} + \frac{\partial}{\partial r}\left[f^s\left(\frac{dr}{dt}\right)^s\right] = 0, \tag{1}$$

$$\frac{d\overline{c_i}}{dt} + \sum_{s_i}\frac{4\pi}{n_0}\int_0^\infty f^s r^2 J_{ri}^s dr = 0, \tag{2}$$

where $f^s(r,t)$ is the size distribution function of the precipitates of the s-th phase at a given moment in time, Σ_{si} denotes summation over all phases containing *the* i-th component, $\overline{c_i}$ is the average concentration of the i-th component in the solid solution at a given moment in time, J_{ri}^s is the flux of atoms of the i-th component that enters (or leaves) of the precipitates of the s-th phase per unit surface area of precipitates with radius r, and n_0 is the number of sites in the matrix per unit volume.

Also, $\sum_{s=1}^{k} n^s - k$ stoichiometric relationships for the fluxes J_{ri}^s , are needed (3):

$$\frac{J_{ri}^s}{\gamma_i^s} = \frac{J_{rd}^s}{\gamma_d^s} \tag{3}$$

where n^s is the number of components in the s-th phase and the subindex d is associated with the d-th component, therefore γ_i^s and γ_d^s are the stoichiometric coefficients of the i-th and d-th component respectively of the s-th phase. These stoichiometric relationships establish the atomic fluxes of components that effectively form (or dissolve) the elementary cells or elementary entities of the chemical compound (precipitate of radius r) belonging to s-th phase.

On the other hand, let us define to F_{ri}^s as the net flux of atoms of the i-th component that arrives by diffusion close to the surface of precipitate of radius r belonging to the s-th phase; thus, the atoms of this component that can cross the interphase boundary, taking into account the stoichiometric relations (3) of the s-th phase and the interphase particularitities, will define the J_{ri}^s flux. This is given because the F_{ri}^s flux will only depend on the atomic mobility of the components and on the concentration gradients of the components in the matrix [16–17], whereas the J_{ri}^s flux will besides depend of the stoichiometric relationships (3) in the precipitate (s-th phase) and particularities of the boundary between the matrix and precipitate of the s-th phase. Then, according to this, it should be noticed that the condition $F_{ri}^s \geq J_{ri}^s$ has to be satisfied for each component of the s-th phase. Thus, all atoms that arrive (or go away) by diffusion close to the precipitate surface should not necessarily enter (or leave) to the same one.

The ratio of F_{ri}^s with the corresponding stoichiometric coefficient γ_i^s will give the rate per unit area of the greatest quantity of elementary cells or entities that could be formed, with the i-th component in the precipitate of radius r belonging to the s-th phase, supposing that sufficient atoms of the remaining components can enter the precipitate. It is easy to see that each component has a different value of this ratio in the same phase. Thus, we define the component that controls the s-th phase growth to that ratio having the smallest rate to form elementary cells. Therefore, this component will be denoted by the sub index d in advance. Then, it can be written as:

$$\frac{F_{rd}^s}{\gamma_d^s} < \frac{F_{ri}^s}{\gamma_i^s} \tag{4}$$

In other words, only the component that controls the s-th phase growth (controller component) will have assured enough atoms of the remaining components to form actually $\frac{F_{rd}^s}{\gamma_d^s}$ elementary cells (or elementary entities) per second and per unit area of precipitate. According to the above, $F_{rd}^s = J_{rd}^s$. It can be noticed that the controller component could change in the course of the decomposition diffusive because that F_{ri}^s depends on time; that is to say, a phase could have different controller components during the competitive growth in time.

Now, allow us to designate to a component of each phase that satisfies the following relation $\frac{Q_m}{\gamma_m^s} < \frac{Q_i}{\gamma_i^s}$ with the m subindex. Here Q_i is the all quantity of atoms of the i-th component in the system formed by the solid solution and precipitates. The $\frac{Q_i}{\gamma_i^s}$ ratio gives the amount of elementary cells (or elementary entities) that could be formed of the s-th phase with Q_i atoms of the i-th component supposing that enough atoms of the remaining components exist.

When the phases do not have components in common, the true quantity of elementary cells that can be formed corresponds to the smaller $\frac{Q_i}{\gamma_i^s}$ ratio, or with the $\frac{Q_m}{\gamma_m^s}$ value. On the contrary, when phases have some components in common, the real quantity of the elementary cells or entities that can be formed will depend of these common components. This latter situation will be now treated.

To simplify the analysis, we particularize in a n-component system with k-phases and only one component in common (denoted by the c sub index) among the phases. Firstly, if a relation like (5) is satisfied:

$$\frac{Q_c}{\sum_{s=1}^{k}\left(\gamma_c^s \frac{Q_m}{\gamma_m^s}\right)} \geq 1, \tag{5}$$

Then, it means that sufficient atoms of the common component