Simulation of phase transitions in multiphase systems: peritectic solidification of $(RE)Ba_2Cu_3O_{7-x}$ superconductors

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Abstract

The phase-field concept as an efficient tool to describe microstructure evolution is briefly reviewed and its extension to multi-phase systems is highlighted. The method has been applied to simulate several features occuring during the peritectic growth of YBCO superconductors. The respective results contribute to the understanding of the growth mechanisms and reveal a dissolution/reprecipitation mechanism contributing to 211 particle displacement leading to inhomogeneous 211 particle distributions. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Knowledge about the mechanisms occuring during the solidification of materials is most useful to improve both their production process and their properties, as in the case of high temperature superconductors (HTS), e.g. their rate of production or their critical current density, J_c.

Numerical simulations in recent years have gained more and more importance in materials science and especially the simulation of microstructure evolution has become a rapidly growing field of scientific and commercial interest. Different techniques are used in this context, such as interface tracking algorithms, molecular dynamics simulations based on a Monte Carlo-like approach, cellular automata techniques and phase-field simulations. Each of these approaches has its advantages and disadvantages which are mainly related to computational efficiency and scale of application. The phase-field concept allows the description of microstructure evolution on a mesoscopic scale and its governing equations can be derived directly from fundamental Ginzburg–Landau physics of phase transitions. Phase-field is a method to treat free boundary problems without keeping track of the local position of the interface.

The scope of the present paper is to briefly review the principal ideas of the phase-field concept as well as its extension to multi-phase equilibria and to demonstrate its potential using different examples of phenomena being observed during the peritectic growth of $(RE)Ba_2Cu_3O_{7-x}$ HTS.

2. The phase-field concept

In order to describe phase transitions in a system containing N different phases which may transform into each other, in the phase-field concept, N functions $\Phi_1(\check{x},t)...\Phi_N(\check{x},t)$ are defined indicating the vol.% of each phase being present at time t in an infinitely small volume centered at point $\check{x}$.

Naturally, the following constraint is imposed

$$\sum_{\alpha=1}^{N} \Phi_\alpha(\check{x},t) = 1 \quad (i.e.100\%).$$

To describe the evolution of the microstructure, knowledge is required about the change of all fractions $\Phi_\alpha(x,t)$ in time, i.e. the knowledge of N partial differential equations for the time derivatives $\dot{\Phi}_\alpha(x,t)$.

For a two phase system such as a solid (s) to liquid (l) transition where $\Phi_s + \Phi_l = 1$, a phase-field equation has first been solved numerically by Kobayashi [1],

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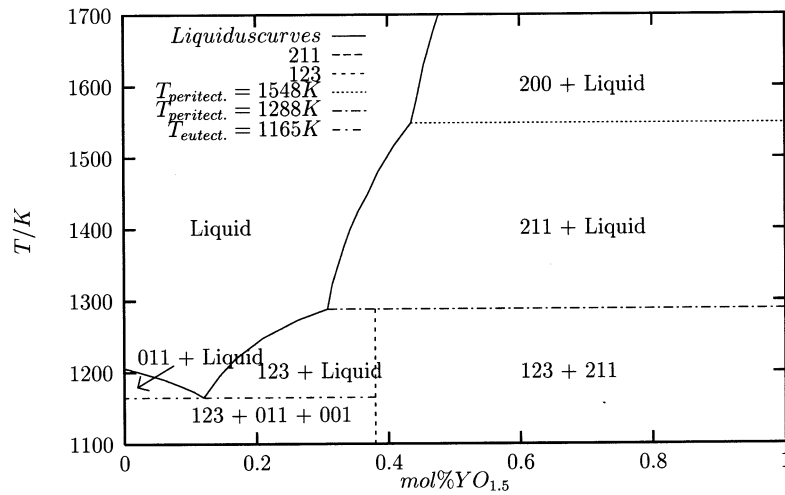[1] Present address: Foundry Institute, Aachen University of Technology.

Fig. 1. Phase diagram of the Y–Ba–Cu–O system along the Y_2BaCuO_5 –$YBa_2Cu_3O_7$–$BaCuO$–CuO tie line. Simulations have been made slightly above the peritectic temperature T_p to study coarsening effects and slightly below T_p to investigate peritectic reactions/transformations.

$$\tau \dot{\Phi}_s(x,t) = \varepsilon \, \nabla^2 \, \Phi_s(x,t)$$

$$+ \frac{1}{a} \, \Phi_s(x,t)(1 - \Phi_s(x,t))(1 - 2\Phi_s(x,t))$$

$$+ \frac{m}{a} \, \Phi_s(x,t)(1 - \Phi_s(x,t)),$$

where ε and a are coefficients essentially related to interfacial tension and interface thickness, respectively, τ is a relaxation parameter and m corresponds to an external driving force dependent on temperature and/or concentration. This equation is derived from a free energy functional using variational principles and its solution for the stationary case ($\dot{\Phi} = 0$) and absence of an external driving force ($m = 0$) is a hyperbolic tangent function describing a stationary interface in equilibrium. Introducing an external driving force, e.g. an undercooling ΔT ($m \neq 0$), the solution becomes time dependent and its shape corresponds to the stationary solution but now moving with a velocity v in space.

This motion can, in solid/liquid phase changes, be identified with a moving solidification front and then has to be coupled to the release of latent heat, which is proportional to the rate of phase change $\dot{\Phi}$. In the case of alloys also, the segregation of solute has to be considered. This release of latent heat, or the segregation of solute, leads to changes in the conditions for the driving force m for the evolution of the phase fields. Accordingly, the entire system can be described by a set of differential equations for the phase fields, mutually coupled with the well known diffusion equations for temperature and solute fields. A detailed review on the phase-field concept describing phase transitions in dual-phase systems (e.g. solid↔liquid) can be found in [2].

Most real systems in metallurgy reveal the co-existence of more than the two phases, solid and liquid, e.g. systems consisting of two solid phases α and β and a liquid L. Specific examples are eutectics, where a liquid L at the eutectic temperature T_e transforms into two solid phases α and β ($L \rightarrow \alpha + \beta$) or peritectic systems, where a solid phase β grows by dissolution of another solid phase α in the liquid L ($L + \alpha \rightarrow \beta$) at the peritectic temperature T_p. To account for such situations, the phase-field concept has recently been extended to the description of multi-phase systems [3]. The basic idea of this extension is to describe the evolution of an entire system of three (or more) phases e.g. (α, β, L) by the sum of the evolutions of all dual boundaries, i.e. (α,β) ($\alpha,$L) ($\beta,$L) and to neglect any contributions from a higher order, e.g. from a trijunction order.

This multi-phase-field concept could be proven to yield the well known relations for the force equilibria at triple junctions (Young's law, Herring torque terms) in
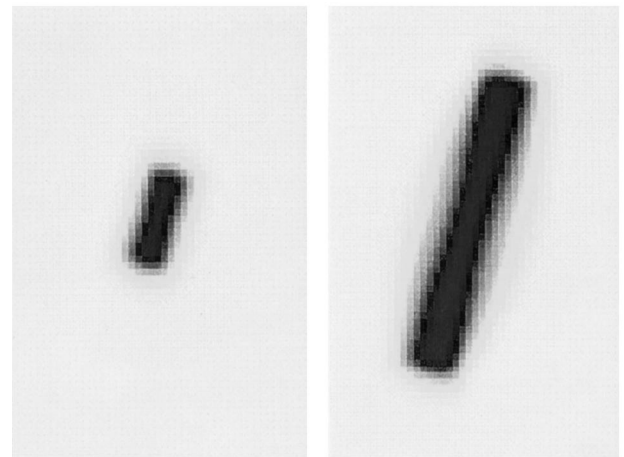

Fig. 2. Simulations of two anisotropically growing 211 particles. Lower diffusion constants and/or higher interfacial energies lead to a more pronounced anisotropic shape of the particles. The aspect ratio strongly exceeds the anisotropy of the growth velocities, which has been set $v_a = 2v_c$ in both cases.
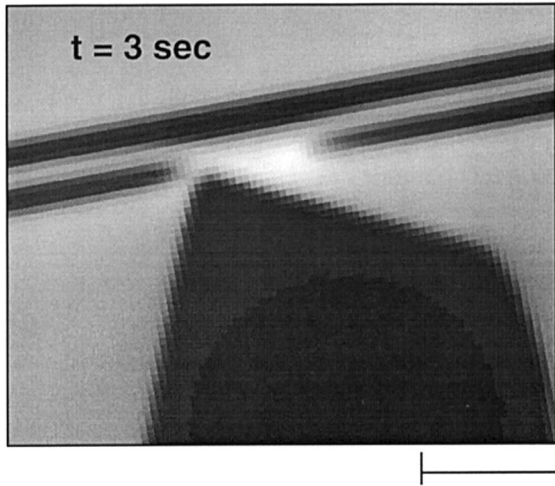
Fig. 3. Dissolution and fragmentation of a properitectic 211 needle ahead of a growing peritectic 123 crystal. Note that dissolution does not predominantely take place at the regions of highest curvature, i.e. the needle tips, but at the closest distance between 211 and 123 crystals.

a sharp interface limit by mathematical analysis [4,5]. Numerical simulations also recover these classical laws in the diffuse interface situation [6].

The multi-phase-field concept and especially the coupling of the phase-field evolution to external fields have been verified for a eutectic microstructure, where analytical solutions are available for special cases [7].

3. Simulations of peritectic solidification of $Y_1Ba_2Cu_3O_{7-x}$

The multi-phase-field concept has been applied to investigate features of YBCO growth numerically in
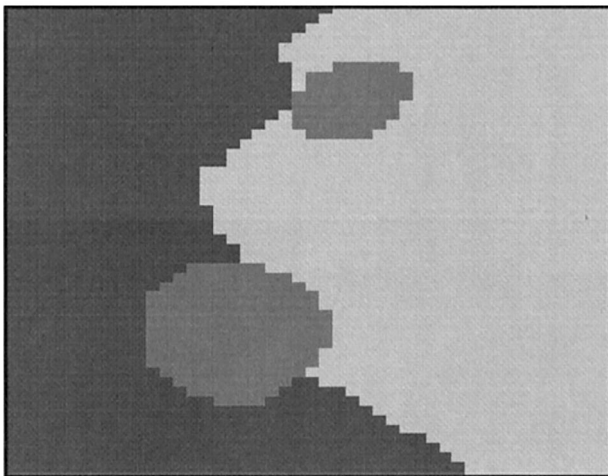

Fig. 4. A high concentration of solute promotes growth of the 123 phase in the vicinity of dissolving 211 particles leading to the formation of bridges.
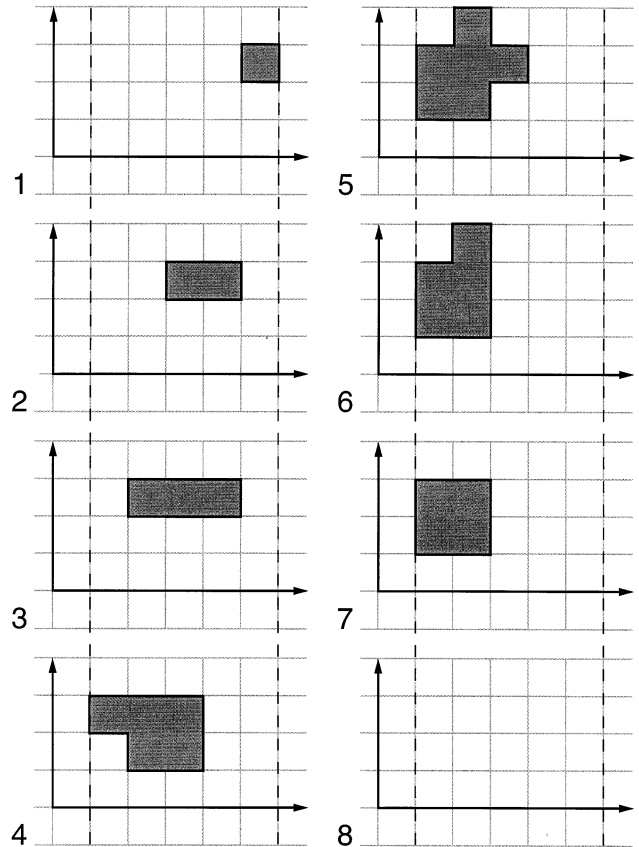

Fig. 5. A particle ahead of a peritectic solidification front (not shown, growing from right to left). Note the motion of the particle relative to the grid in combination with coarsening and final (8) dissolution. This appearant motion is due to a dissolution/reprecipitation process.

order both to understand the growth mechanisms and to improve the solidification processes.

The simulations are based on a pseudo binary cut of the quaternary phase diagram along the BaCuO–CuO–$Y_2Ba_1Cu_1O_5$ (211)–$YBa_2Cu_3O_7$ (123) tie line, Fig. 1, and have been carried out isothermally at two specific temperatures: (i) slightly above the peritectic temperature in the region $(L + 211)$ to investigate coarsening phenomena of the 211 particles and (ii) slightly below the peritectic temperature to study peritectic reactions and transformations $(L + 211 \rightarrow 123)$.

All calculations assume the diffusion of yttrium to be the rate determining factor for the transformation. Other diffusion fields (e.g. Ba, Cu, O) have not been implemented.

Computations in general have been carried out in two dimensions on a numerical grid and aimed to investigate following effects:

- coarsening of 211 phase: isotropic/anisotropic particles
- influence of doping/surface tension, Fig. 2
- formation of needles
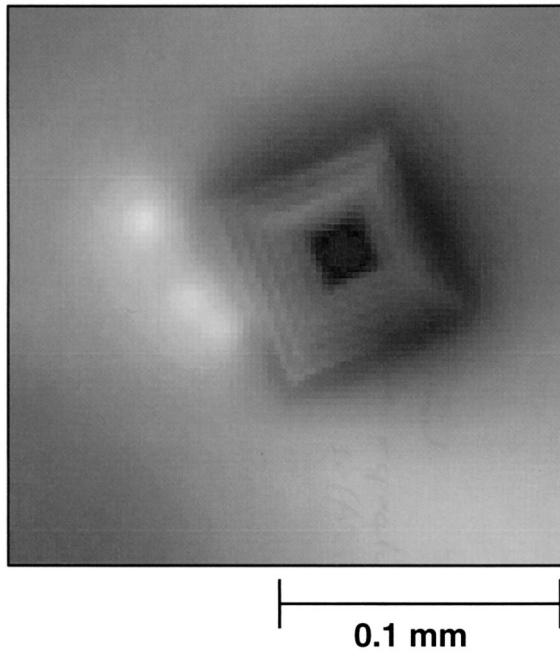- dissolution of 211 ahead of a growing 123 front: peritectic reaction/transformation, Fig. 3

Fig. 6. x-like segregation patterns of yttrium solute in a 123 crystal growing from dissolving 211 particles. The high yttrium content at the corners makes the 211 particles more stable at these locations in contrast to locations at the facets of the 123 crystal. This corresponds to a higher ratio between engulfment and dissolution probabilities at the corners.

- bridge formation at low G/R, Fig. 4
- anisotropic coarsening
- particle pushing, Fig. 5
- growth of a $YBa_2Cu_3O_{7-x}$ domain in a multi-parti-

cle ambient: formation of x-like patterns, Fig. 6
- competitive growth of several 123 grains: grain selection, Fig. 7
- texture formation

These simulations qualitatively recover experimentally observed phenomena, e.g. like needle growth of 211 particles, bridge formation, desintegration and fragmentation of 211 needles, x-like patterns [7–10] and indicate the mechanisms of pushing/engulfment of 211 particles to be related to a dissolution/reprecipitation mechanism [11].

4. Conclusions

Many phenomena of $(RE)Ba_2Cu_3O_{7-x}$ growth can be modelled qualitatively using the multi-phase-field concept even though the calculations are still restricted to one-component diffusion. In special cases, like particle pushing, simulations contributed to the clarification of the origin of specific effects. The future inclusion of oxygen diffusion and its effects on the formation of the superconducting phase are worth investigating. This, however, will require the implementation of the real quaternary phase diagram as an electronically stored data set.

Such a link between electronically accessible thermodynamic databases and the phase-field software will allow for further optimization, not only of HTS, but also of many other technologically important alloys and composites.
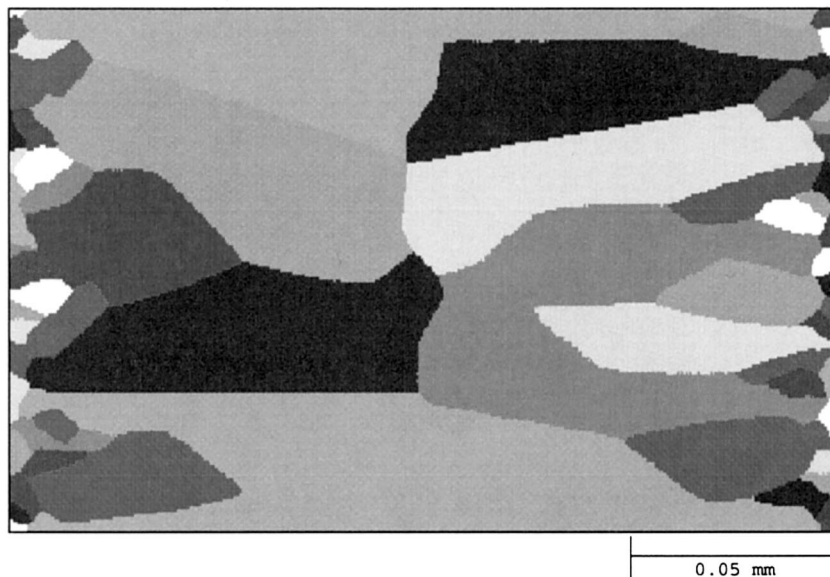

Fig. 7. Grain selection mechanism acting between differently oriented grains of 123 growing from a homogeneous liquid. The grain selection leads to a textured microstructure being beneficial with respect to superconducting properties.

Acknowledgements

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