EQUILIBRIUM MICROSTRUCTURE FORMATION DURING PRESSURE-INDUCED PHASE TRANSITION

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Pressure-induced phase transitions in closed pressure cells reveal some pecularities in their kinetic behaviour: Because of the isochoric boundary conditions, the transition may terminate before the lower dense phase is completely transformed. The accompaning pressure depletion modifies significantly the microstructure of the evolving nucleation and growth process (cluster size distributions).

Keywords: phase transitions, microstructure formation, diamond anvil cell

INTRODUCTION

The study of the stability fields of several mineral phase systems in dependence of p,T has attracted considerable attention over decades of years. More recently it was recognized, that in addition to the knowledge of the phase diagram the detailed investigation of the transition kinetics itselves may give some deeper insight even into the equilibrium properties of the different phases [1]. In the case of pressure-induced transitions, mainly transformations of first-order type occur. Hence, the study of the kinetics of nucleation and growth processes is of increasing importance in high-pressure mineral physics.
One of the most excellent tools for in-situ studies of structural phase transitions is the diamond anvil cell (DAC). The direct visibility of the on-going processes allows for in connection with an image processing system the quantitative analysis of the arising spatial microstructures in dependence of time [2,3].
However, since the sample volume in the DAC is very small (of the order of 10^{-12} m^3), the transition kinetics is considerably influenced by the pressure depletion during the transition in the cell. In addition, the plastic deformation of the gasket material may lead to a further modification of the observed physical process kinetics with an external given kinetic law. A correct interpretation of the obtained kinetic data is therefore needed.
In this paper we present a method to model these different influences on the formation of microstructures during first-order phase transitions. A numerical simulation technique is used to compute the cluster size distribution in dependence of

time, and the obtained results are compared with experimental observed microstructures during the precipitation of the B2-phase of potassium iodide KI from supersaturated solution in the DAC.

EXPERIMENTAL

The apparatus consisting of a DAC combined with a image-processing system is described elsewhere [2]. The principle of the optical determination of the evolving microstructures is based on the measurement of the proportion between the two phase areas derived from their differing refractive indices. To achieve hydrostatic conditions, a metal-foil gasket with a small hole filled with the pressure-transmitting medium is placed between the anvils. As a consequence of the setup, only a 2D projection of the transition process is detectable.
In the first stage of nucleation, the nuclei of B2-phase KI crystals originate homogeneously distributed over the sample volume, indicating good hydrostatic conditions. They continue to grow at small overpressures Δp in a stable faceted form according to their cubic structure, until in the final stage the process is slowly terminated in consequence of the accompaning pressure depletion in the cell ($\Delta p \rightarrow 0$).

MODEL CONCEPTION

Nucleation and growth processes are commonly described by a continuity equation in cluster space for the radii distribution function n(r,t) of the (spherical assumed) nuclei at time t [4]:

$$\frac{\partial}{\partial t} n(r,t) = - \frac{\partial}{\partial r}\left[Y(r,t)\, n(r,t)\right] + j(r,t) \qquad (1)$$

with

$$I^V(t) = \int_0^\infty j(r,t)\, dr \qquad (2)$$

and appropriate chosen boundary conditions.
Here, the growth rate Y(r,t) and the nucleation rate $I^V(t)$ are in general two arbitrary functions given by the basic physical processes driving the phase change; the time dependencies of both rates are due to possibly existing external variations of the thermodynamic conditions p,T. According to eqs. (1) and (2), the arising microstructure is a unique function of Y and I^V. Our aim is now to convert the problem into the question: How can we deduce from a given (measured) microstructure some informations about the nature of Y and I^V ?

MODIFIED AVRAMI EQUATION

By setting $Y(r,t)=Y_0(t)$ and $j(r,t)=I^V(t)\,\delta(r)$ it follows from eqs. (1) and (2) the modified Avrami equation

$$x(t) = 1 - \exp\left\{ - (4\pi/3) \int_0^t I^V(t')\left[\int_{t'}^t Y_0(t'')dt'' \right]^3 dt' \right\} \qquad (3)$$

for the volume fraction x(t) of the new phase.

Eq. (3) may be transformed into a set of four coupled ordinary differential equations, which can easily be solved by standard Runge-Kutta methods. It must be appended with a further independent equation describing the time development of the thermodynamical variables p or T. In our experimental situation it follows from the isochoric boundary condition

$$p(t) = p_r(t) - c\,x(t)\,, \qquad (4)$$

where $p_r(t)$ contains the explicit time dependence of pressure due to the external gasket relaxation and c is a constant depending on the preparation [3,5].
However, the computation of the arising microstructures on the basis of eqs. (3) and (4) is practically impossible. We have therefore developed a simple simulation procedure to model the nucleation and growth process by the help of a high resolution graphics card of a personal computer.

SIMULATION PROCEDURE

The use of the PC graphics card allows for the correct modeling of the spatial digitization due to the CCD matrix video camera, and it essentially simplifies the needed analysis of the generated microstructures. This is a significant advantage in comparison with simulation approaches of other authors [6].
The simulation is organized as follows: Critical nuclei of the high-pressure phase are randomly generated in the initially homogeneous metastable phase with rate I^V, and they grow afterwards with linear velocity Y on the screen. Both quantities I^V and Y are calculated from a suitable thermodynamical formula via eqs. (3) and (4) for the actual p,T-conditions in every Runge-Kutta time step [7]. Once a growing crystal is crossing a lattice point, the corresponding pixel is setted on the VGA screen, see Figure 1.

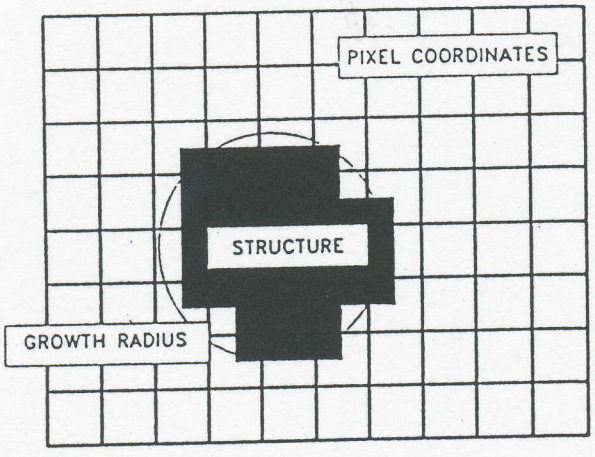

Figure 1
Simulation of nucleation and growth processes on a graphics card of a personal computer

If different nuclei impinge each other during their growth they form increasingly larger cluster, thereby inhibiting growth at their common interface. The arising microstructures, which are strongly dependent on Y and I^v, are continuously stored as binary data files on the computer hard disk and can afterwards be analyzed by standard image processing software.
In order to show their essential influence on the forming cluster size distribution, two different (limiting) growth mechanisms are considered [4]:

1. "interface controlled growth"
   The growth velocity is limited by the time needed to incorporate a unit into the developing surface.
   $$Y_{IF} = c_1 \qquad (c_1 \text{ .. constant}) \qquad (5)$$

2. "diffusion controlled growth"
   The limiting process at the developing crystalline surface is the long-range transport of units to the interface.
   $$Y_{DL} = c_2 \text{ / crystal radius} \quad (c_2 \text{ .. constant}) \qquad (6)$$

A detailed description of the simulation alorithm is given in [5].

RESULTS AND DISCUSSION

The shapes of the generated cluster size distributions are shown in Figure 2 with a transformed volume rate in the order of 10%:

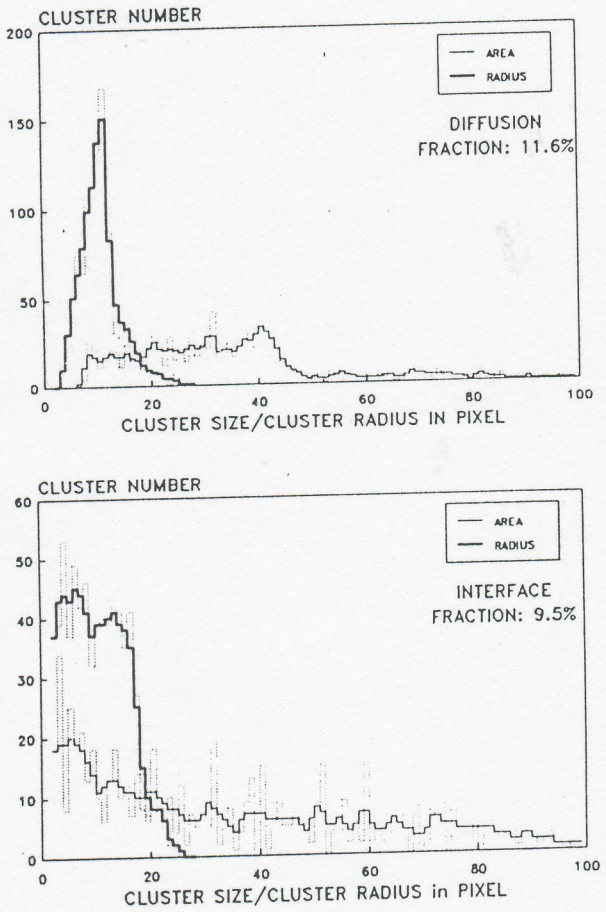

Figure 2
Simulated cluster size distributions vs. cluster area and cluster radius, respectively.
Case (1): lower chart
Case (2): upper chart
The solid lines represent the results with a smoothing correction

In case (1), the distribution is approximately rectangular, whereas in case (2) a sharp maximum is formed at a certain cluster size. The reason for this triangular form including a maximum is obviously the strong enhancement of the growth rate Y for small crystals according to eq. (6). Therefore one can find out by inspection of the stored data files, at which transformation stage which growth mechanism is going on.
If we compare the experimental sequences of the precipitated high-pressure B2-phase crystals, then they seem to confirm our earlier conclusion that there is a cross-over behaviour in the growth mechanisms between interface and diffusion controlled growth: The best fit is found with an "intermediate" growth type [3,5] of the form

$$Y_{IM} = c_1 + c_2 / \text{crystal size} \quad , \tag{7}$$

compare Figure 3.

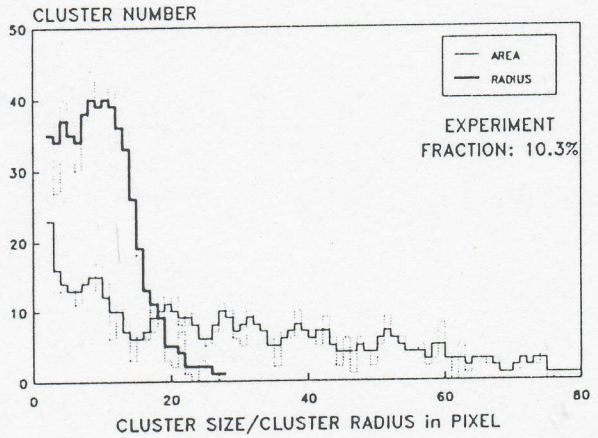

Figure 3
Comparison between an experimentally detected cluster size distribution and a simulated distribution with an intermediate growth rate according to eq. (7).
The solid lines represent again the results with a smoothing correction

CONCLUSIONS

It is shown that the microstructure formation in first-order phase transitions is sensitively dependent on the type of growth mechanism. For two limiting cases we find decisive differences in the shape of the generated cluster size distributions. From an experimental point of view it should therefore be possible to decide (with the aid of a image processing system) which type of growth mechanism is dominant in the phase transition of interest. In the special case of a selected high-pressure precipitation reaction in the diamond anvil cell it is found a best coincidence for an intermediate growth type.

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Proceedings of the
XIII AIRAPT International Conference on High Pressure Science and Technology

7-11 October 1991

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Edited by
Anil K. Singh