

Modelling the evolution of vein microstructure with phase-field techniques – a first look

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ABSTRACT Vein microstructures in the Earth's crust contain a wealth of information on the physical conditions of crystal growth, but correct interpretation requires an improved understanding of the processes involved. In this paper the processes involved in the formation of veins are briefly reviewed, and the possibilities of modelling these processes using the phase-field method are discussed. This technique, which is established in the computational materials science community to investigate crystallization processes, is shown to be a powerful tool to describe processes during vein formation and other geological processes involving crystal growth.

Key words: crystal growth; microstructure simulation; phase-field method; vein.

INTRODUCTION

Veins are subplanar discontinuities in the Earth's crust, containing minerals which precipitated from a supersaturated solution in a fracture (Urai *et al.*, 1991). They are common structures, formed under a very wide range of conditions. Their widths can vary from less than a millimetre to tens of metres (Cox & Etheridge, 1983; Oliver & Bons, 2001). Veins are often associated with ore deposits or hydrocarbon accumulations, and can be of major economic importance. Recent interest in geothermal systems and the coupling of thermal, mechanical, hydraulic and chemical processes in rock masses (e.g. Yow & Hunt, 2002; Fischer *et al.*, 2003) has emphasized the need for a better understanding of the processes which seal fractures in a rock mass.

The minerals in veins contain information on the conditions of their formation. There are a number of main classes of data which can be used to solve this inverse problem. First, minerals frequently contain fluid inclusions from which the crystals grew in the past. These fluid inclusions can be analysed using a range of techniques to obtain information on the pressure, temperature and impurity content of the fluid at the time of crystal growth (Grawinkel & Stöckhert, 1997). Second, the coexisting minerals in veins constrain the P – T conditions of their formation to the parts of the phase diagram where the phases are stable. Third, the isotope chemistry of vein minerals can in some cases be used to deduce the age of the vein or even the duration of the growth phase (Elburg *et al.*, 2002; Lee *et al.*, 2003). Finally, the microstructure of veins can be used to infer the direction of opening of the fracture, the opening trajectory, the permeability

of the system during crystallization, and perhaps even palaeo-overpressure or palaeo-seismicity (e.g. Durney & Ramsay, 1973; Cox, 1987; Urai *et al.*, 1991; Wiltschko & Morse, 2001; Hilgers & Urai, 2002; Nollet *et al.*, 2005; Nuchter & Stöckhert, 2007).

PHENOMENOLOGICAL MODELLING OF VEIN FORMATION

In this paper, we focus on the vein microstructure. There is a large literature documenting the wide variability of microstructures in veins (Bons, 2000). Relatively simple microstructures consist of single-phase polycrystals, grown from the walls of a fracture towards the centre. In these veins the low-index crystal facets developed by the growing crystals can sometimes still be recognized.

Other veins may show much more complex and enigmatic microstructures. One well-known type is the so-called fibrous vein: here the crystals have morphologies which are dramatically different from what would be expected for growth in a free fluid (Hilgers & Urai, 2002). The crystals are highly elongated, and may even develop curved shapes which are a consequence of growth, not deformation (Hilgers & Urai, 2005; Cox, 1987; Urai *et al.*, 1991; Bons & Bons, 2003) (Fig. 1).

Urai *et al.* (1991) developed a kinematic, phenomenological model for crystal growth in crack-seal veins and showed the importance of the wall rock morphology for the resulting microstructure. Urai *et al.* (1991) showed that the repeated contact between the crystals and the wall rock has a strong effect on the microstructures. If the crystals have sealed the space available before the next crack event, they lose their facets and assume the morphology of the rough vein

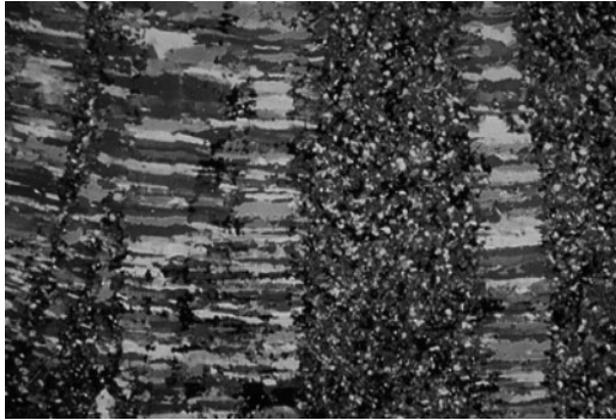


Fig. 1. Micrograph of a thin section of fibrous veins of quartz in sandstone, Eifel, Germany. These veins are usually interpreted as having formed by a large number of delocalized crack-seal events, producing the so-called stretched crystals. Made with crossed polarized light, width of image is 2 mm.

wall interface. If opening increments are sufficiently small, the crystals cannot develop crystal facets and grow isotropically (Hilgers *et al.*, 2001). The result of isotropic growth is that the grain boundaries will grow towards peaks in the wall rock. This control of the grain boundaries by wall irregularities depends on the angle between the incremental opening vector and the local orientation of the crack surface. An important element of the model proposed by Urai *et al.* (1991) was the assumption that the crystal growth kinetics are effectively isotropic if the crack surface is sufficiently rough. To include anisotropic growth, the numerical simulation program **VEIN GROWTH** was developed. It simulates the kinematics of crystal growth under complex boundary conditions and can simulate crack-seal growth with an incremental opening trajectory. The transition from a faceted crystal to an isotropic growing crystal, due to the interference with the wall rock, can also be simulated with this algorithm. Simulations with **VEIN GROWTH** produced fibrous crystals in a vein with the potential to track the opening trajectory of the crack when the wall morphology is rough and the average opening velocity is smaller than the growth velocity of the crystals. In simulations of a natural microstructure, full tracking was achieved with opening increments smaller than 10 μm , of the same order as the inclusion band spacing in natural crack-seal veins (see Hilgers *et al.*, 2001; Becker *et al.*, 2003; Jessel, Bons, 2002; Nollet *et al.*, 2005a,b; Bons *et al.*, 2008).

Experimental simulation of the evolution of veins has been notoriously difficult (Lee *et al.*, 1996; Hilgers *et al.*, 2004). This is caused by the fact that supersaturated fluids have to be generated and transported, leading to unstable conditions.

In summary, although existing models can produce rather natural-looking microstructures (Nollet *et al.*, 2005a,b), the models are still very simple, and do not incorporate many of the basic thermophysical and

continuum mechanics concepts which govern the phase transition dynamics underlying the vein formation process. The most essential challenges to be met by a satisfactory model of vein growth (in addition to the fracture formation processes) in the Earth's crust are summarized in Fig. 2: here we consider an inert 'wall rock' – a porous, permeable but non-reactive material which contains the vein: a polycrystal under conditions where the crystals can grow from a supersaturated solution. This polycrystal is in contact with a fracture containing a supersaturated solution which may or may not be in motion. The fracture may be quite wide (10 m) or extremely thin (1000 nm). The crystals have not yet been capable of developing facets, so that all interfaces are irrational. The model should be capable of correctly describing the transport of dissolved material (diffusion or advection), the crystal growth kinetics as a function of supersaturation, the development of facets on the growing crystals, the propagation of grain boundaries, and the final stages of sealing the fractures.

CONTINUUM DYNAMIC MODELLING OF VEIN FORMATION

From a continuum mechanics and thermodynamic point of view, the above requirements result in a model

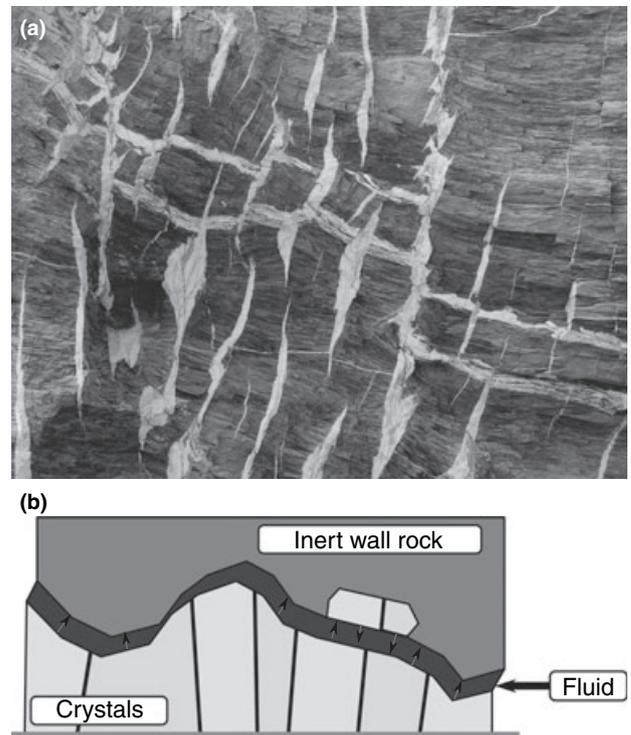


Fig. 2. (a) Veins of calcite in shale, Wadi Yikah, Oman. Width of image is 3 m. (b) Schematic picture of the main processes of vein formation. It shows the vein which has developed a new fracture partly along the wall rock–vein interface, and partly through some of the grains in the vein. During crystallization from a supersaturated solution which may or may not be moving, the grain boundaries and grain surfaces propagate until the fracture is sealed, forming facets under the right conditions.

which extends the general rigorous mathematical model approaches for crystallization. It is given by the following set of equations.

Transport of solute

$$\frac{\partial C}{\partial t} = D_C \nabla^2 C. \quad (1)$$

This equation models the transport of dissolved species in the liquid phase. In a first approach the main governing, i.e. growth-limiting, transport processes are assumed to be diffusive. Thus C denotes the number of solute particles per volume element of the liquid and D_C the mobility of these particles. Later in this section hydrodynamic transport is included as well.

Interface kinetics

$$C = \Delta - d\kappa. \quad (2)$$

This equation is the well-known Gibbs–Thompson relation which has to be evaluated at the interface between the polycrystal and the supersaturated solution. In this equation, Δ is the non-dimensional supersaturation and d an anisotropic capillary length proportional to the free energy of this interface. Depending on the crystal symmetry, this interface also inherits a symmetry, e.g. a fourfold one if the polycrystal has fcc symmetry. Then $d(\theta)$ is given as

$$d(\theta) = d_0(1 - \varepsilon_4 \cos 4\theta), \quad (3)$$

where θ denotes the angle between the global growth direction and the local normal direction at the respective point along the interface.

ε_4 is a constant factor quantifying the strength of the anisotropy.

The $1 - \varepsilon_4 \cos 4\theta$ part of the above equation is the *anisotropy function*, and in this form represents one of the most simple and common types used in modelling the growth of crystals with fourfold anisotropy. The basic shape of the resulting crystal (in the absence of diffusion and other influences) depends on the Wulff shape (for examples of Wulff shapes and how to construct them, as well as alternate anisotropy functions, see Uehara & Sekerka, 2003). The simple form of this anisotropy function makes it easy to use and calculate in simulations, and depending on the value of ε_4 chosen the Wulff shape can vary from a perfect circle ($\varepsilon_4 = 0$) to a near square with somewhat rounded edges (high ε_4 values). This anisotropy function is given as just an example – different anisotropy functions can be used to represent a large range of different crystal symmetries and shapes as they can be observed in veins.

Propagation of grain boundaries

$$v_n = -[D_l \vec{n} \cdot \vec{\nabla} C]. \quad (4)$$

This final equation is the Stefan condition. It yields the normal velocity at which the crystal is growing into the oversaturated solution and follows from mass and energy considerations.

If the solution is in motion, the hydrodynamic transport has to be modelled as well. This is achieved by coupling the above set of equations to the incompressible Navier Stokes equations, given as follows.

Hydrodynamics of the liquid phase

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u}, \quad (5)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (6)$$

where ν is the viscosity, p the pressure field and ρ the density of the liquid phase. Moreover \mathbf{u} denotes the vector indicating the velocity of the flow field in all space directions.

Now the full set of equations describing the crystallization of a polycrystal in the surrounding supersaturated liquid is given by Eqs (1)–(6). Note that if hydrodynamic transport in the liquid phase is taken into account, Eq. (1) changes to also include a convective part, which is as follows.

Transport of solute with convective contribution

$$\frac{\partial C}{\partial t} + (\mathbf{u} \cdot \nabla) C = D_C \nabla^2 C. \quad (7)$$

NUMERICAL IMPLEMENTATION OF THE MODEL

The physical foundation underlying the above model equations is the following: the transport of the dissolved species is in a first approximation mainly a diffusive one. Thus, it is natural to model it with a diffusion equation as given by Eq. (1). To solve such a diffusion equation boundary conditions have to be imposed. One boundary condition follows from the assumption that the transport field relaxes more or less instantaneously to the growing interface of the polycrystal. This is certainly well justified in geological crystallization processes as vein formation, which develops on a comparatively large time-scale. The assumption formulated here yields the Gibbs–Thompson relation, i.e. Eq. (2) of the above model. It also implies that the system is assumed to be locally at thermodynamic equilibrium.

Globally, however, the system is not at equilibrium. Rather growth of the polycrystalline interface is encountered, which is connected with a phase transition, i.e. a non-equilibrium process. This process has to

be formulated taking mass and energy conservation properly into account, which finally yields Eq. (4).

The above formulation is known as the sharp-interface formulation of the crystallization problem. To solve such a problem in a numerically efficient way, the phase-field method was established in computational materials science community over the last two decades. The phase-field method eliminates one of the problems tied inherently to the above formulation, which is the need to resolve the interface separating the polycrystal and the surrounding liquid explicitly at each time step of the evolution. It does so via the introduction of an additional order parameter field, i.e. the phase field, which varies smoothly over the interface and serves as an identification function of the different phases throughout the evolution. Besides allowing for an efficient numerical scheme, which is easy to parallelize via domain decomposition, it also has the great advantage of directly linking the model to the phase diagram of the crystal system under observation, as it is fully based on a thermodynamic variational approach. This allows for a fully quantitative comparison to experiments. Therefore, the phase-field approach has established itself successfully over the past two decades for problems of the above kind (e.g. Langer, 1986; Chen & Khachatryan, 1991; Wang *et al.*, 1993; Kobayashi *et al.*, 2000; Emmerich, 2009). In particular, it proved to be a very powerful approach for studying front evolution problems – as in growing veins – under multiphysical influences (Emmerich, 2003b; Emmerich & Siquieri, 2006), often accompanied by the formation of several distinct phases (Emmerich & Siquieri, 2006; Siquieri *et al.*, 2007) or grains of multiple orientations (Assadi, 2004; Hubert & Emmerich, 2005) and interactions of different governing mechanisms over several time and length scales (Emmerich *et al.*, 2004; Eck & Emmerich, 2006).

In the following a phase-field model is adapted for the vein formation set-up outlined at the end of third section. We simulate the resulting model equations and thereby give a visual first impression that the phase-field method certainly has the capacity to establish itself as a valuable computational approach for non-equilibrium processes in geological systems such as the formation of veins. At this point the results are purely qualitative. More quantitative studies are in progress.

PHASE-FIELD MODEL AND SIMULATION RESULTS

Our phase-field model corresponding to the above sharp-interface formulation without taking into account hydrodynamic contributions is based on three parameters: the phase field ϕ and the solute field C , as well as the orientation order parameter θ .

The differential equations for ϕ and C can be derived from the free-energy functional (Emmerich, 2003a; Assadi, 2004; Hubert & Emmerich, 2005):

$$F = \int \left[g(\phi, C) + \frac{1}{2} \varepsilon^2 |\nabla \phi|^2 + \frac{1}{2} v^2 \phi^2 G(|\nabla \theta|) \right] dV. \quad (8)$$

Here ε and v are constant values, G is an operator depending on the local symmetries of the crystal, and $g(\phi, C)$ is the local energy density, represented by a fourth-order polynomial function (for details, see Assadi, 2004).

From this energy functional, the model equations for the phase field and the concentration field are derived as partial differential equations (see Wheeler *et al.*, 1993):

$$\frac{\partial \phi}{\partial t} = -M_\phi \frac{\delta F}{\delta \phi}, \quad (9)$$

$$\frac{\partial C}{\partial t} = \nabla M_C \nabla \frac{\delta F}{\delta C}. \quad (10)$$

Additionally, the phase-field variable is prevented from decreasing once a specific computational cell reaches solidification. This represents the irreversible nature of the simulated physical processes (at least within the context of the conditions we want to examine).

Unlike the phase field and the concentration field, the evolution of the crystal orientation θ is calculated with a Monte Carlo algorithm. Initially, each solid nucleus is assigned a specific crystal orientation. Each liquid cell in the simulation grid is assigned a random orientation θ out of a finite number of possible equidistant orientations. In each calculation step, a new random orientation θ_{new} is chosen, again out of the same finite number of possible orientations. A probability p is then calculated which determines if the orientation θ_{old} switches to θ_{new} :

$$p = M_{\text{GB}} \left[1 - \exp\left(\frac{E_{\text{mis}}(\theta_{\text{new}}) - E_{\text{mis}}(\theta_{\text{old}})}{kT}\right) + \xi \right]. \quad (11)$$

M_{GB} is a general grain boundary mobility factor for the solid–liquid boundary. ξ is a ‘noise’ term representing thermal fluctuations. The mismatch energy E_{mis} is calculated as follows:

$$E_{\text{mis}} = \sum_i (F(\theta) - F(\theta_{\text{new}})). \quad (12)$$

As only θ changes, only the $\frac{1}{2}v^2\phi^2G(|\nabla\theta|)$ part of the energy functional remains. The equation thus can be written as:

$$E_{\text{mis}} = \sum_i \frac{1}{\Delta r_i} \frac{1}{2} v^2 \eta_i^2 [\sin(|\theta_{\text{new}} - \theta_i|) - \sin(|\theta_{\text{old}} - \theta_i|)]. \quad (13)$$

The sum is added up over all calculation cells within a specific radius ‘rad’, with the exception of the currently examined cell. Δr_i is the distance from the

currently examined cell. η is an order parameter introduced in Kobayashi *et al.* (2000) which represents the general ‘structuredness’ of any given region, with a value of 1 representing complete structuredness (i.e. the bulk of a crystal) and 0 representing complete lack of structure (i.e. a liquid). This was simplified by Assadi (2004) and folded into the phase-field parameter – which is a reasonable approximation, as the solid–liquid differences measured by ϕ also represent how ‘ordered’ a region is. However, this simplification turned out to be insufficient for examining the growth of crystals at triple point boundaries and resulted in errors stemming from the layout of the calculation grid. Therefore, η was reintroduced. It is defined as follows:

$$(\eta \cos \theta, \eta \sin \theta) = \frac{1}{N} \sum_i^N (\cos \theta_i, \sin \theta_i) \quad (14)$$

For the purposes of the simulation, the definition of η was expanded by an additional limitation. This is because in the liquid ‘regions’ of the simulation, the random nature of the orientations used meant that η according to this term would rarely be truly ‘unstructured’ – i.e. attaining a value of 0 (at higher resolutions, the random fluctuations would gradually even themselves out, as more calculation cells would be used to calculate for any given η values, but the computational effort for such vastly higher resolutions would be highly unreasonable for the intended purpose). Fortunately, ϕ already defines liquid regions through its own value, which operates on the same scale as η . To properly represent liquid regions with η , any values of η for any given calculation cells are set in a way so that they never exceed ϕ for the same cell.

Figures 3 and 4 show the results of a first qualitative study of grow competition. A number of grains with random orientations were seeded at the bottom of the calculation field consisting of 400×400 cells. These grains were then allowed to grow into a solute. The surface anisotropy function was chosen so as to produce a square single crystal with slightly rounded corners when growing in a free fluid. The diffusion coefficient was chosen to be very high, to allow the formation of strong facets.

As can be seen in Fig. 3, the individual grains with different orientations have partly rounded and partly faceted morphology, go through a process of growth competition and develop curved grain boundaries under the influence of capillary, kinetic and long-range forces.

Figure 4 shows the concentration distribution in the liquid. For this simulation, D_C was set to identical values for liquid and solid, but this does not need to be the case – the diffusion constants can be set to differ between liquid and solid. Diffusion could also be switched off for the solid entirely, depending on what kinds of phenomena and growth processes the simulation is intended to model. Here, the high diffusion

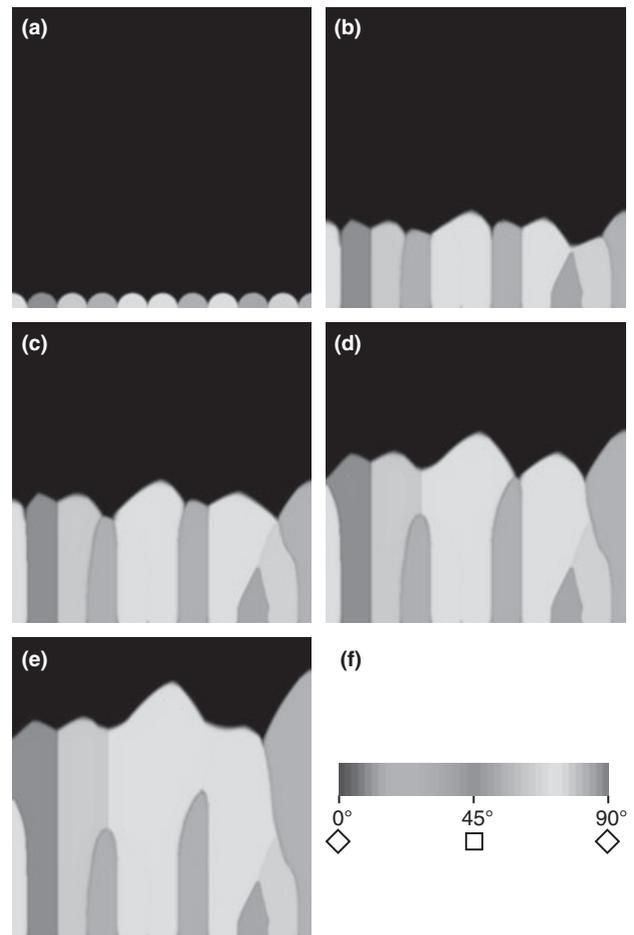


Fig. 3. Phase-field simulations of vein formation (qualitative) after (a) 0, (b) 50 000, (c) 100 000, (d) 150 000 and (e) 200 000 time steps. Different levels of brightness represent different orientation of the crystals as shown in the orientation bar (f). Black area is solute.

constant coupled with the equal diffusion constants result in low concentration values at the most pronounced tips, as the imbalances in the concentration field caused by the solidification can quickly diffuse away into the liquid at these locations.

While this study was quantitative, it represents the growth of crystals with random orientation in real vein formation processes quite well. In contrast to the comparatively fast solidification processes more commonly examined in phase-field simulations, a significantly higher diffusion constant was used here – which represents the fact that over the process duration of vein formation, the solute will be thoroughly mixed, resulting in few spatial variations of the solute concentration. This results in the only slightly rounded tips of the growing crystals (compare with the strongly rounded tips visible in figs 5 & 6 in Emmerich, 2003b). Crystals growing in veins are usually strongly faceted. Achieving such tips through simulation should be possible by using more complex (and thus, more computationally intensive) anisotropy functions whose

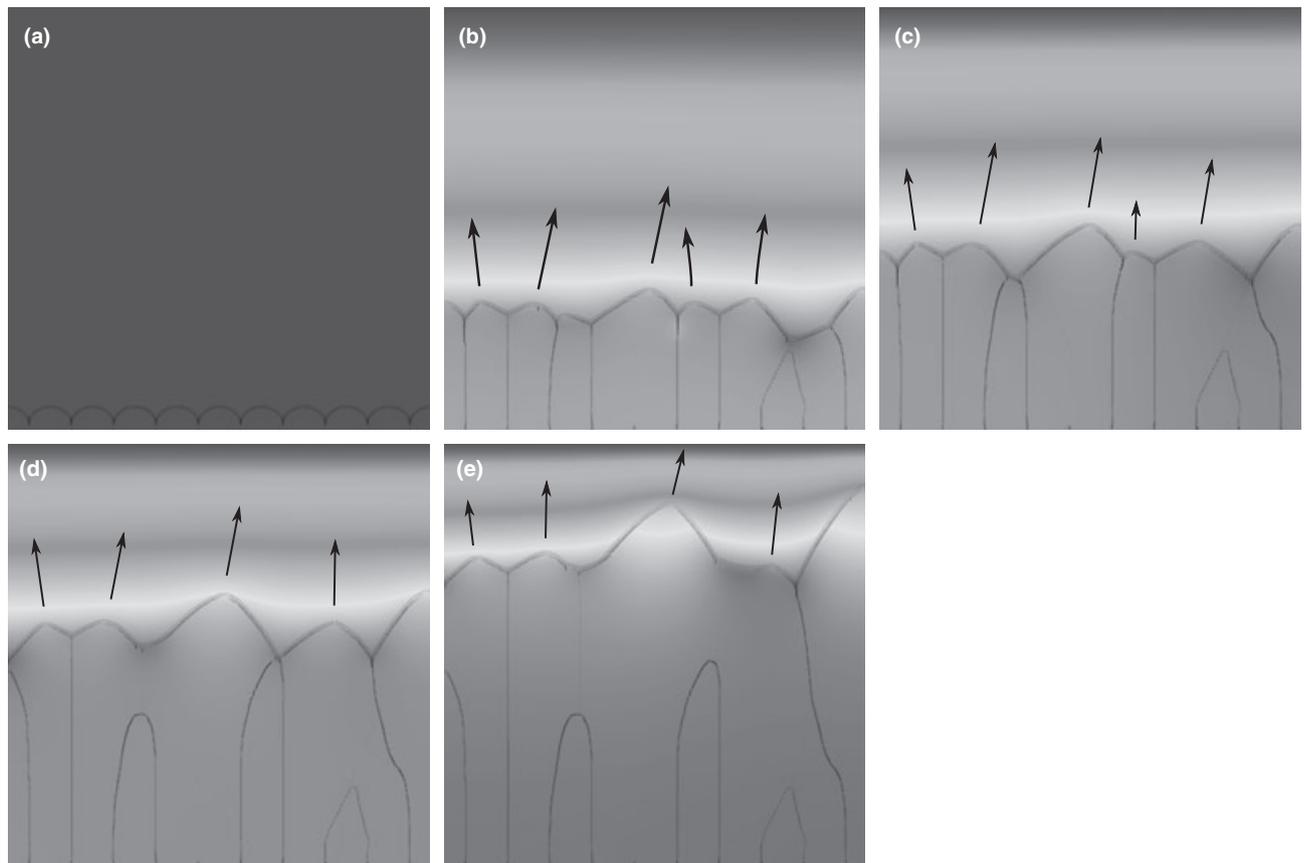


Fig. 4. The corresponding concentration field after (a) 0, (b) 50 000, (c) 100 000, (d) 150 000 and (e) 200 000 time steps. The different levels of brightness represent different temperature zones, ranging from the hottest region at the bottom to the coolest at the top.

Wulff shapes have strongly pronounced tips (for an example, see Uehara & Sekerka, 2003) and even higher diffusion constants, better representing the extremely long time spans involved in this type of crystallization process.

As can be seen here, the individual grains with different orientations go through a growth competition which takes place in the bulk under the influence of capillary, kinetic and long-range forces. The crystals whose anisotropy are more closely aligned with the direction facing the saturated liquid ultimately grow faster and crowd out the crystals whose anisotropy is less advantageously aligned.

CONCLUSIONS AND OUTLOOK

Here we have introduced a phase-field model to simulate the geological process of vein formation. To do so, the expertise which has established itself in the computational materials science community since the early 1980s, has been exploited to model and simulate similar crystallization processes. The underlying model equations are based on continuum mechanical and thermodynamical concepts, and resolve the full non-linear dynamics of the phase transition underlying the

vein formation process dynamically into the governing physical field. Thus the model deserves further investigation, which will eventually allow us to understand the basic mechanisms of vein formation in full detail.

Several expansions to the model, such as the removal of diffusion in the solid, a higher complexity anisotropy function will permit more pronounced tips, and choosing even higher diffusion constants are expected to model crystal growth processes in veins even more accurately and can be added with relatively little programming effort (although they will require significantly more computational time to complete simulation runs). Solid walls of matter to represent the rock surrounding the gap can also be added to more accurately portray the local environment in vein formation processes without adding much complexity to the model. Likewise, simulating the growth of crystals from two different directions to represent the sealing of fractures is mostly a matter of using different initial conditions for the program.

The main drawback of phase-field models like this one when compared with other vein-growth models such as those described by Nollet *et al.* (2005a), Koehn *et al.* (2001) or Bons (2001) is that they are

comparatively computationally resource intensive. The requirement to simulate the local values for the phase field, temperature field and orientation field at a resolution high enough to discretize the tips of the microstructure places significant demands on computational power. For example, the phase-field simulation shown in this paper took 6 days to compute on an AMD Opteron CPU with 1.4 GHz. Nevertheless, the flexibility of phase-field models and the ease of extending them for different physical phenomena makes them well suited as a tool worth exploring in this community. For example, further modifications to the model based on existing phase-field models can include hydrodynamic convection (Emmerich & Siquieri, 2005; Siquieri & Emmerich, 2007), as well as stress and deformation (Eck & Emmerich, 2006). Additionally, it is possible to extend the phase-field method from two to three dimensions (Jeong *et al.*, 2001), although doing so represents a significant increase in the required computational time. After these extensions, the model will be the focus of a further reaching parameter study which will be concerned with the precise effect of hydrodynamic convection on the morphology of the growing vein front when advancing on an upper wall at different temperatures in three dimensions. Furthermore, by using appropriately chosen parameters, the method can relatively easily be adopted to model microstructure evolution during crystal growth from magma, or during metamorphic reactions.

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Received 8 August 2008; revision accepted 6 July 2009.