

Crystallization of CaO.SiO₂ in a CaO-Al₂O₃-SiO₂ Melt: Computer Simulations and In-situ Experiments

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ABSTRACT

Partial or full solidification of metallurgical slags occurs in many industrial pyrometallurgical processes. To enhance the fundamental knowledge of this phenomenon, this research focuses on the simulation and in-situ observation of crystallizing minerals in oxide melts. The isothermal crystallization of Wollastonite (CaO.SiO₂) in a ternary CaO-Al₂O₃-SiO₂ melt is investigated. We used a confocal laser microscope (CLSM) to observe the dendritic crystallization and measured the dendrite tip radius and its velocity as a function of undercooling. The phase field method is chosen to model and simulate the crystallization, because it has proven its power for phase transformations in metals. The phase field model uses a vast number of physical input data, such as Gibbs energies of the phases, diffusion coefficients of the components and the interfacial energy of the solid-liquid interface. The thermodynamic data is retrieved from the FACTSage database for oxide systems. Diffusion coefficients are taken from literature, while surface energies are varied through the simulations. By comparing experimental values for the dendrite tip velocity with values obtained with simulations, the influence of surface energy and diffusion coefficients on the crystallization behavior can be assessed.

INTRODUCTION

Crystallization of oxide melts is an important phenomenon in many application domains, such as geology, pyrometallurgy, glass ceramics and advanced ceramic materials. Silicate melts in geological research are mostly referred to as magna or lava, and crystal growth in these melts controls many textural and chemical features of igneous rocks¹. In high temperature metal extraction processes (pyrometallurgy), the silicate melt, resulting from the used ores, is called slag. Crystallization or solidification of such slags influences the behavior of freeze linings of pyrometallurgical reactors², the mineralogy of the cooled slag after tapping³ or the usability of mold fluxed during continuous casting of steel⁴. Moreover, the production of glass ceramics, for example, occurs by controlled crystallization of a heavily undercooled liquid to obtain a glassy material with superior mechanical properties⁵. At last, production of dense parts of refractory ceramics is often done by liquid-phase sintering, in which the crystallization or dissolution of the powder particles in the interconnected liquid plays an important role⁶.

Crystallizing phases often exhibit complex morphologies on the mesoscale, dendrites being a well-known example⁷. The phase field concept has proved to be a very powerful tool⁸ for modeling evolving microstructures. Within a phase field model, the microstructure of a material is described with a set of auxiliary variables, phase fields, which relate to the local phase fractions. Assuming diffuse interfaces at the boundaries of phases, the equations can be solved over the whole system, without prior knowledge of the interface positions. Therefore, a phase

field model can treat arbitrarily complex interface shapes with minimal mathematical complexity.

In this work, we use the phase field method to simulate crystallizing dendrites of Wollastonite in a CaO-Al₂O₃-SiO₂ melt. The phase field model uses a vast number of physical input data, such as Gibbs energies of the phases, diffusion coefficients of the components and the interfacial energy of the solid-liquid interface. The thermodynamic data is retrieved from the FACTSage database for oxide systems. Diffusion coefficients are taken from literature, while surface energies are varied through the simulations. The simulations are compared with experimentally obtained results, using a confocal laser microscope, which allows *in situ* observation of crystallization phenomena at high temperature.

EXPERIMENTAL TECHNIQUE

High temperature crystallization processes can be observed *in situ* using a hot stage confocal laser microscope (CSLM)^{9,10}. This technique offers numerous advantages over classical experimental techniques, in which the sample is quenched after different times¹¹. For example, several isothermal observations can be made in a single experiment and quenching effects, such as phase transformations during cooling, are avoided. The crystallization of Wollastonite is observed *in situ* by seeding the supersaturated silicate melt with Wollastonite itself, which is the primary phase for the considered melt composition. In contrast to adding oxide particles as nucleation sites⁴, intermediate reaction products between the nucleation site and the silicate melt are avoided, which allows a more straightforward interpretation and a more accurate analysis.

The crystallization experiments were done in an infrared (IR) heating chamber combined with a confocal scanning laser microscope (CSLM, Lasertec, 1LM21H-SVF17SP, Japan). A schematic of the equipment is shown in Figure 1. The sample is heated by a 1.5 kW halogen lamp in a focal point of a gold plated ellipsoidal chamber while the sample is in the other focal point. This infrared heating system can reach temperatures up to 1700 °C in a few minutes.

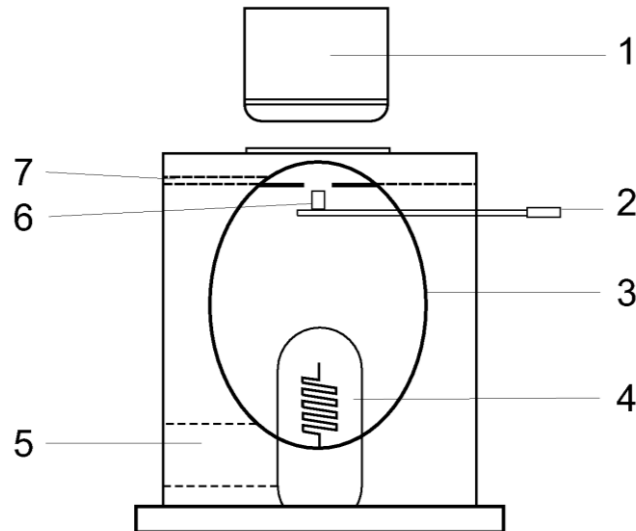


Figure 1: Schematic representation of the high temperature CSLM technique: (1) objective lens of the laser microscope, (2) sample holder with thermocouple, (3) gold plated ellipsoidal chamber, (4) halogen lamp, (5) outlet to the vacuum system, (6) Platinum crucible with sample, (7) inlet for auxiliary gases.

Premelted glass particles are prepared, with the composition: 42wt% CaO, 10wt% Al₂O₃ and 48wt% SiO₂. This glass is melted and quenched in the hot stage of the CSLM, in a Platinum crucible, to obtain a dense glass inside the crucible. At room temperature, a few fibers of Wollastonite (micron size), are put on top of this glass using fine tweezers. Wollastonite is the

primary phase of crystallization for the melt, and, therefore, we expect the growing crystals to be Wollastonite. There is no thermodynamic driving force for other phases to form or grow in the temperature and composition range of the experiments. Furthermore, the nucleation barrier vanishes with the addition of Wollastonite to the melt.

The isothermal crystallization experiment is performed at 1320°C, where Wollastonite crystallizes in dendrite crystals. The dendrite tip velocity is determined manually by drawing auxiliary lines on the micrograph at different times (see Figure 2). A reference line is also drawn to account for possible rotations of the crystal. At every second, the length of the primary dendrite arm, from the reference line to the dendrite tip, is calculated using the correct scaling from the micrograph. Figure 2 shows the result of the analysis, depicting two dendrite tip positions versus time. The dendrite exhibits a constant velocity, as predicted by the Ivantsov theory¹². Using both linear fits, the dendrite tip velocity is determined as $8.4 \pm 0.3 \mu\text{m s}^{-1}$.

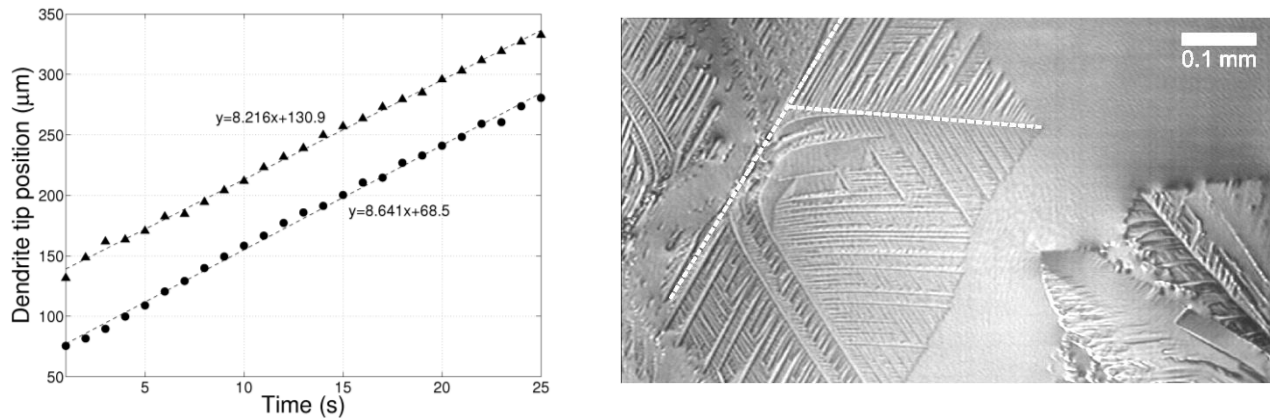


Figure 2: The left graph shows the dendrite tip position versus time for the dendritic crystallization of Wollastonite at 1320°C. Two different tip positions are shown and the equations of the linear fit are indicated in the Figure as well. The dendrite tip velocity is thus determined as $8.4 \pm 0.3 \mu\text{m s}^{-1}$. The right figure shows a micrograph of crystallizing Wollastonite at 1320°C in a $42\text{CaO}-10\text{Al}_2\text{O}_3-48\text{SiO}_2$ melt. The growth form is clearly dendritic with a hexagonal symmetry.

In these experiments, the crystallization starts at the Wollastonite additions, and occurs at the liquid-vapor interface. In recent work¹³, we have shown that the experimental state of the dendrite, with velocity and radius, is situated between the theoretic values of the 2D and 3D theory of Ivantsov. Therefore, we don't expect a perfect agreement with this experiment and 2D simulations of dendrite growth.

PHASE FIELD MODEL

In a phase field model for microstructure evolution, the equations are defined and solved over the whole system without prior knowledge about the position of the interfaces. Microstructure evolution in an isothermal system at constant pressure is driven by minimization of the total Gibbs energy. The microstructure of the system is described by a set of continuous non-conserved phase field variables, η_i , which are related to the local phase fractions. The phase field variables, η_i , are equal to 1 where the respective phase is physically present and 0 elsewhere in the system. At the interfaces in the microstructure, the phase field variables of adjacent phases vary smoothly from 0 to 1 and vice versa. These diffuse interfaces, within a phase field model, allow the equations to be solved over the whole computational domain.

The total energy, F [J], of a heterogeneous isothermal system with p phases and c components is formulated as a functional of the non-conserved phase field variables, η_i , and the conserved concentration variables, x_k :

$$F = \int_V \left[m f_0 + \frac{\kappa}{2} \sum_{i=1}^p |\nabla \eta_i|^2 + \sum_{i=1}^p \phi_i f^i \right] dV$$

The first two terms in the integrand, $m f_0 + \frac{\kappa}{2} \sum_{i=1}^p |\nabla \eta_i|^2$, are responsible for the diffuse character of the interfaces. Furthermore, the parameters m and κ are uniquely related to the surface energy, σ_{ij} [Jm^{-2}], of the interfaces. These parameters have an orientation dependency when the interfaces have crystalline (or weak) anisotropy. The third term, $\sum_{i=1}^p \phi_i f^i$, is the contribution of the Gibbs energies of the phases, f^i [Jm^{-3}], to the total system energy, where ϕ_i is the phase fraction¹⁴. In conclusion, the equation above expresses the total energy of the system, including both the interfacial and bulk energies.

According to the principles of linear non-equilibrium thermodynamics, the microstructure is assumed to evolve in such a way, to allow the largest energy dissipation¹⁵. Therefore, the evolution equation for each phase field variable, η_i , follows a time-dependent Ginzburg-Landau equation for non-conserved variables,

$$\frac{\partial \eta_i}{\partial t} = -L \frac{\delta F}{\delta \eta_i}$$

where L is related to the mobility of the interfaces. When the interfaces exhibit strong (or faceted) anisotropy, L is heavily dependent on the orientation, resulting in slowly growing crystal orientations that define the growth form of the crystal. Next to these phase field equations, a set of diffusion equations is solved. The diffusion equation for each of the $c-1$ independent components is given by¹⁶:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[\sum_{i=1}^p \phi_i \left(\sum_{l=1}^{c-1} M_{kl}^i \nabla \tilde{\mu}_l^i \right) \right]$$

where x_k is the mole fraction of component k . The elements M_{kl}^i form a mobility matrix \mathbf{M}^i for phase i , which relates to the interdiffusion matrix \mathbf{D}^i and thermodynamic factors matrix \mathbf{G}^i according to the following formula:

$$\mathbf{D}^i = \mathbf{M}^i \mathbf{G}^i \quad G_{r,s}^i = \frac{\partial \tilde{\mu}_r^i}{\partial x_s^i} = \frac{\partial^2 f^i}{\partial x_r^i \partial x_s^i}$$

SIMULATION SETUP AND RESULTS

Numerical implementation

The phase field and diffusion equations are discretized on an equidistant numerical grid using central finite differences, in the FORTRAN programming language. The boundary conditions (Neumann or periodic) are implemented using ghostnodes at the border of the numerical domain. The program code is parallelized and executed on a High Performance Computer cluster using 100 processors for two-dimensional simulations. To increase the numerical efficiency, the phase field equations are only solved in the proximity of interfaces, while the diffusion equations are solved everywhere. The implementation was validated with several cases of anisotropic interfaces in equilibrium or analytical solutions to phase transformations in ternary systems.

Simulation parameters

All the parameters of the phase field model, except the numerical width of the diffuse interfaces, can be linked to physical quantities. The Gibbs energy of the liquid phase is retrieved from the FACT thermodynamic¹⁷ database using ChemApp¹⁸. For the Gibbs energy of the stoichiometric solid (Wollastonite), a special parabolic Gibbs energy function is constructed, for compatibility with the phase field concept¹⁹. This Gibbs energy function ensures the correct thermodynamic solid-liquid equilibrium. The diffusion matrix of the liquid phase is taken from literature²⁰. No literature data was found, regarding the solid-liquid interfacial energy. However, the anisotropy of the interfacial energy is set to sixfold, as observed in the experiments (see Figure 2).

Simulation setup

Due to the hexagonal symmetry of the Wollastonite dendrite, the simulations are performed on one fourth of the physical system. The simulation domain is 2000x2000 grid points, which is equivalent to 25x25 μm . In the bottom left corner, a nucleus of Wollastonite is placed (12 grid points in radius) by setting $(\eta_1 = 0, \eta_2 = 1)$ and $(x_{\text{CaO}}, x_{\text{Al}_2\text{O}_3}) = (0.499, 0.002)$. The rest of the simulation domain is liquid phase, $(\eta_1 = 1, \eta_2 = 0)$, with a composition of $(x_{\text{CaO}}, x_{\text{Al}_2\text{O}_3}) = (0.455, 0.06)$, which lies in the Wollastonite-liquid two-phase region at 1320°C. Hence, the liquid is supersaturated and Wollastonite will isothermally grow into the liquid.

Dendritic crystallization of Wollastonite

Several large-scale simulations of dendritic crystallization of Wollastonite are performed. The (unknown) solid-liquid interfacial energy is varied from 0.3 to 1.5 Jm^{-2} . A typical simulation result, for $\sigma_{\text{SL}}=0.3 \text{ Jm}^{-2}$, is presented in Figure 3, by plotting the concentration profiles of the independent components, CaO and Al_2O_3 .

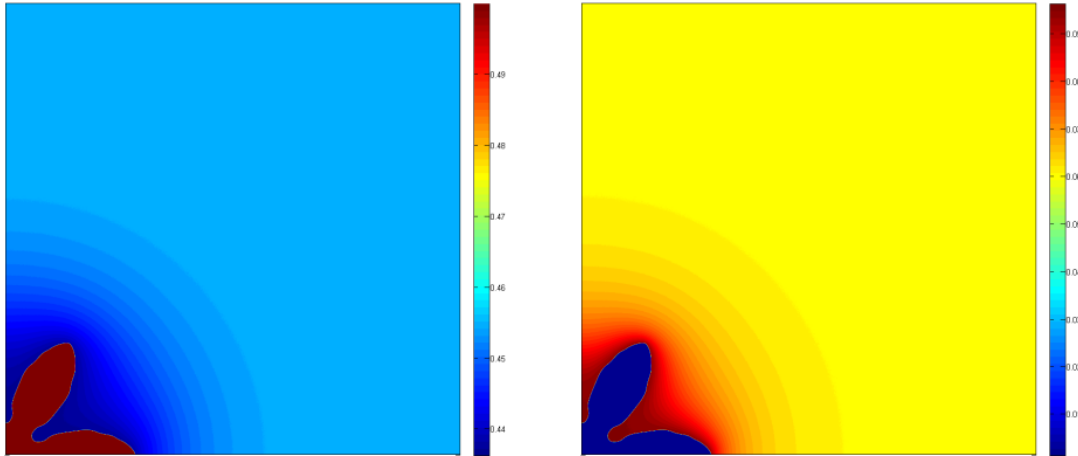


Figure 3: The left figures show the concentration profiles of respectively CaO and Al_2O_3 , around a growing dendrite of Wollastonite. Because of the hexagonal symmetry of the crystal, only 1/4th of the system is simulated.

The dendrite velocity, as function of the interfacial energy, is computed from the phase field profiles and the result is plotted in Figure 4. This Figure shows that the decreasing dendrite tip velocity, with increasing surface energy, cannot reach the experimental value. Therefore, the influence of the mobility matrix of the liquid phase is investigated by scaling the interdiffusivities matrix from 100% to 20% of the literature values, for $\sigma_{\text{SL}}=0.9 \text{ Jm}^{-2}$, for which the results are indicated with squares. It is clear that that a 20% decrease in mobility matrix, brings the simulation result much closer to the experimental value. This observation has led us to investigate the original paper with diffusion data²⁰ more carefully and, indeed, there were serious errors detected in the $D(T)$ expressions, in the abstract of the original paper. An erratum will be

published soon on this matter²¹. The correct diffusion matrix was determined to be about 20% smaller than the originally published one. Taking this into account, the agreement between simulation and experiment is quite satisfactory. However, it should be noted that an exact agreement is not possible due to the different dimensional constraints in the experiment and the simulation. The Wollastonite dendrite in the experiment grows under conditions between 2D and 3D, while the simulation is purely 2D.

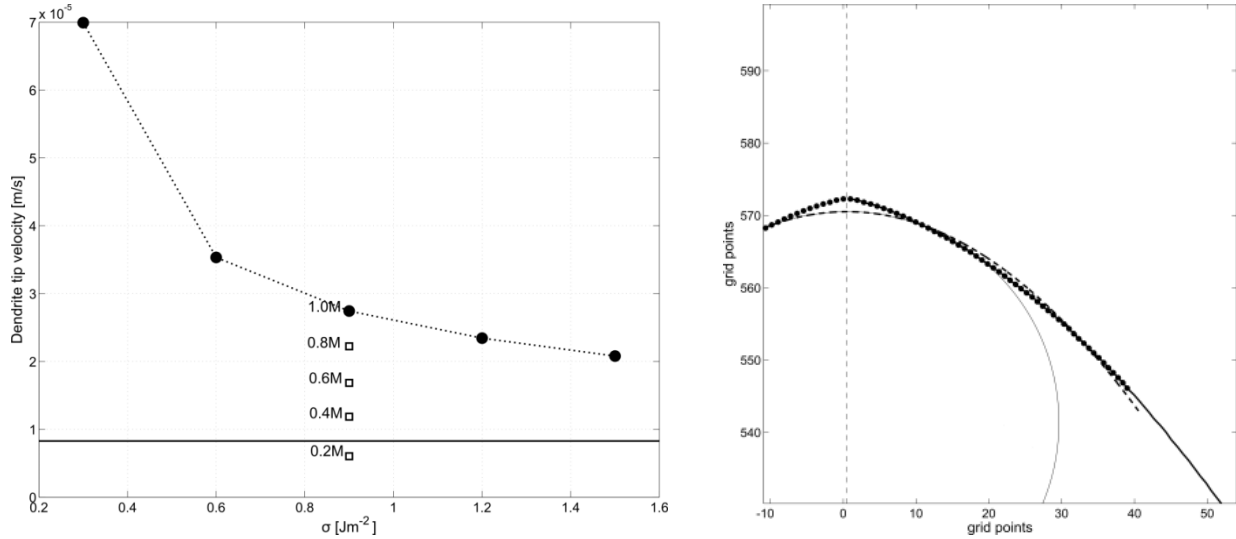


Figure 4: The figure on left shows the relationship between the solid-liquid surface energy and the velocity of the dendrite tip. There is a clear decrease in dendrite tip velocity with increasing surface energy, although this trend cannot reach the experimentally observed velocity of $8.3 \mu\text{m/s}$ (solid line). The right figure shows how the dendrite tip properties are derived from the phase field profiles. The solid line is the 0.5 phase field contour, from which the black dots are taken as data points for the analysis. Through these points, a second order polynomial is fitted, of which the equation is used to determine the tip position and the tip radius.

CONCLUSIONS

We presented a phase field model that is able to describe isothermal crystallization of stoichiometric solid phases in oxide melts. The thermodynamic functions in the model are retrieved from the FACT database for oxide systems using ChemApp. The Gibbs energies of stoichiometric phases are constructed assuming a paraboloid composition dependence. This model is used to simulate dendrite crystallization of Wollastonite in a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt. The influence of both the solid-liquid interfacial energy and the diffusion in the liquid, was investigated. Furthermore, an experimental technique is introduced to observe *in situ* the isothermal crystallization of minerals in silicate melts at elevated temperatures. In contrast to previous research, the primary phase itself, *in casu* Wollastonite, is added to the melt to avoid intermediate reaction products. In the experiments, the crystallization occurs at the liquid-vapor interface, which is neither 2D nor 3D. Therefore, a direct comparison between simulation and experiments is not possible, although the order of magnitude is well predicted.

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