

# Isothermal crystallization of slags: *in-situ* experiments and computer simulations

Jeroen Heulens, Bart Blanpain, Nele Moelans

Dept. of Metallurgy and Materials Engineering, K.U.Leuven

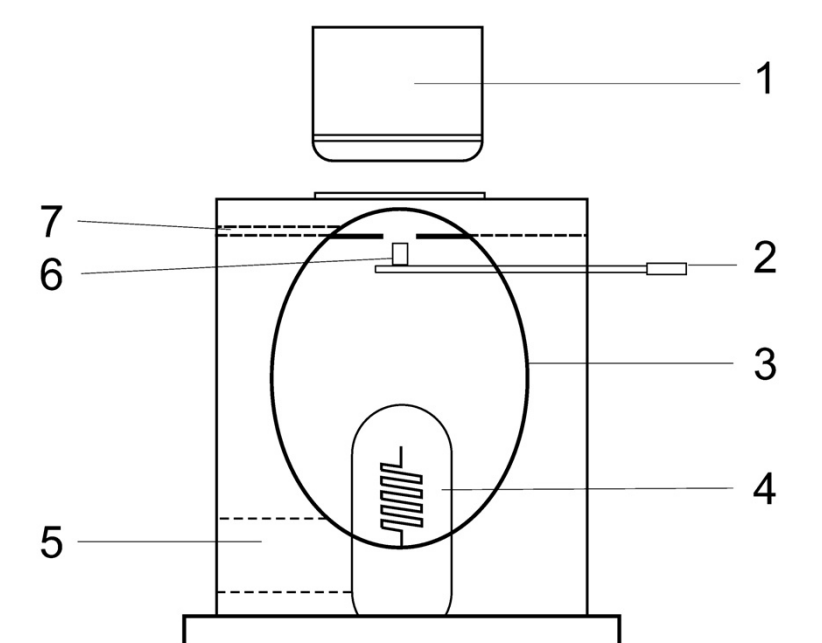
KATHOLIEKE UNIVERSITEIT  
**LEUVEN**

## Abstract

To enhance the fundamental knowledge of slag crystallization, this research focuses on the computer simulation and *in-situ* observation of crystallizing minerals in oxide melts. We used a confocal laser microscope (CLSM) to observe isothermal crystallization of minerals. The phase field simulation technique uses a vast number of physical input data, such as Gibbs energies of the phases (FactSage), diffusion coefficients of the components (literature) and the interfacial energy of the solid-liquid interface (unknown). By comparing experimental values for the mineral growth velocity with simulated values, the influence of surface energy on the crystallization behavior can be assessed.

## Experimental Technique

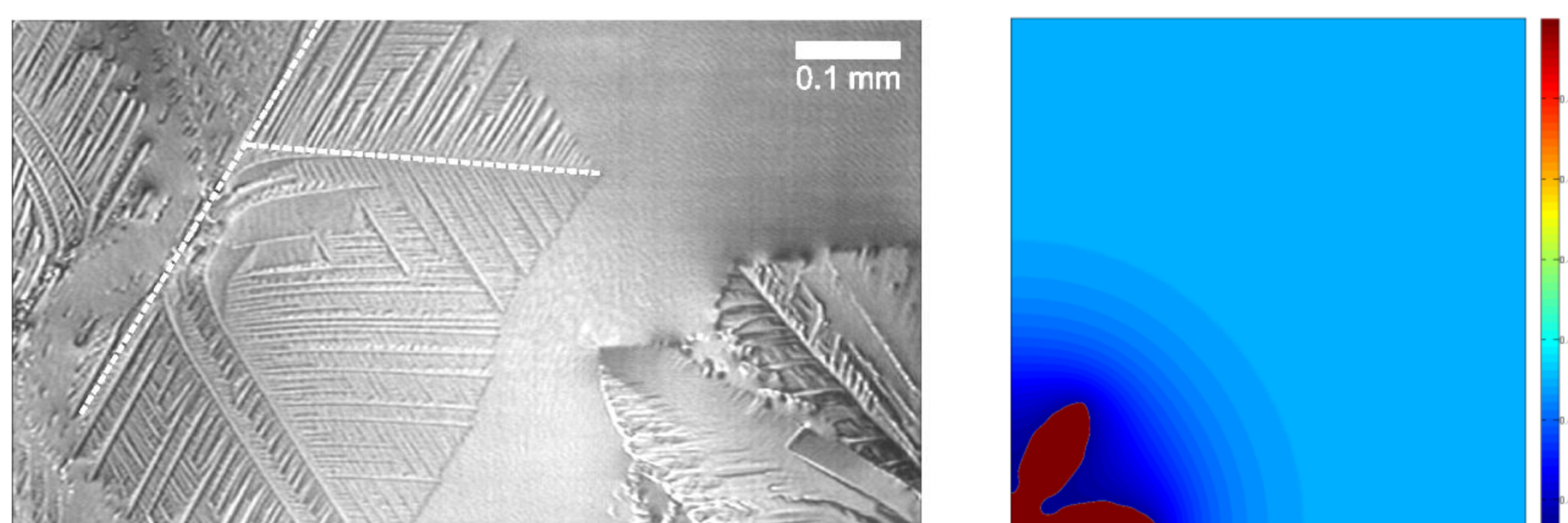
The crystallization is observed real-time in a confocal scanning laser microscope, which is equipped with a hot stage. The sample is heated by a halogen lamp using focal optics. For the considered composition, the primary phase itself is added to the melt in order to avoid intermediate reaction products between other nucleating agents and the melt. The presented technique allows observing the crystal growth morphology and velocity at different temperatures in a single experiment.



**Figure 1:** CSLM technique overview (1) objective lens of the 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.

## Results

The crystallization of wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ) is observed in a super-saturated  $42\text{CaO}-12\text{Al}_2\text{O}_3-48\text{SiO}_2$  melt, where wollastonite is the primary phase for the considered melt composition.



**Figure 2:** Isothermal crystallization of wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ) in a  $42\text{CaO}-10\text{Al}_2\text{O}_3-48\text{SiO}_2$  melt at  $1320^\circ\text{C}$ . The left figure shows the experimental result while the figure on the right presents a typical simulation result (CaO concentration field). The experimental dendrite tip velocity is determined at  $8.4 \pm 0.3 \mu\text{m s}^{-1}$  [3].

Using the computer simulations, the effect of the solid-liquid interfacial energy can be explored. The results are listed in Table 1, which shows a clear decrease in tip velocity with increasing interfacial energy,  $\sigma_{\text{SL}}$ . Furthermore, the order of magnitude compares well with the experimental result. It should be noted that the simulations are 2D, while the surface crystallization in the experiment is either 2D nor 3D.

**Table 1:** Simulated 2D dendrite tip velocities as a function of  $\sigma_{\text{SL}}$ .

	$\sigma_{\text{SL}}=0.3 \text{ Jm}^{-2}$	$\sigma_{\text{SL}}=0.6 \text{ Jm}^{-2}$	$\sigma_{\text{SL}}=0.9 \text{ Jm}^{-2}$
Tip velocity	$4.1 \mu\text{m s}^{-1}$	$2.3 \mu\text{m s}^{-1}$	$1.4 \mu\text{m s}^{-1}$

## Simulation Technique

The phase field technique is a versatile tool for simulating microstructure evolution in materials. We developed a multi-phase and multi-component model to simulate isothermal crystallization in silicate melts [1,2]. The interfaces are assumed to be diffuse and an auxiliary phase field variable  $\eta_i$  is assigned to each phase of the system. The microstructure evolves due to minimization of the total system energy  $F$ :

$$\frac{\partial \eta_i}{\partial t} = -L \frac{\delta F}{\delta \eta_i} \quad F = \int_V \left( m f_0(\eta_i) + \frac{\kappa}{2} \sum_{i=1}^p |\nabla \eta_i|^2 + \sum_{i=1}^p \phi_i f^i(x_k) \right) dV.$$

In the current model, the local energy density consists of an interfacial (first two terms in the integrand) and bulk chemical contribution (third term in the integrand). The model parameters  $m$  and  $\kappa$  are related to the interfacial energies,  $\sigma_{ij}$ , and  $f^i$  are the Gibbs energies of the phases. Next to the phase field equations a diffusion equation is solved for each independent component:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ \sum_{i=1}^p \phi_i \left( \sum_{l=1}^{c-1} M_{kl}^i \nabla \tilde{\mu}_l^i \right) \right] \quad D^i = M^i G^i \quad G_{r,s}^i = \frac{\partial \tilde{\mu}_r^i}{\partial x_s^i} = \frac{\partial^2 f^i}{\partial x_r^i \partial x_s^i}$$

where the mobilities matrix  $M$  is related to the interdiffusion matrix  $D$  through the thermodynamic factor matrix  $G$ . The program code is parallelized and run on a computer cluster.

## Conclusions

- ✓ An isothermal, multi-phase and multi-component phase field model for crystallization of slags
- ✓ An experimental technique to observe the growth morphology and velocity of a primary phase in a slag
- ✓ The simulated and experimental results are of the same order of magnitude

## References

- [1] Heulens J., Blanpain B. & Moelans N., *A phase field model for isothermal crystallization of oxide melts*. Acta Materialia 59 (5), 2156-2165 (2011).
- [2] Moelans N., *A quantitative and thermodynamically consistent phase-field interpolation function for multi-phase systems*. Acta Materialia 59 (3), 1077-1086 (2011).
- [3] Heulens J., Blanpain B. & Moelans N., *Analysis of the isothermal crystallization of  $\text{CaSiO}_3$  in a  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  melt through in-situ observations*, Journal of the European Ceramic Society, In press (2011).