Phase field modelling of the attachment of metallic droplets to solid particles in liquid slags: Influence of particle characteristics

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ABSTRACT

Metallic droplets can be attached to solids in slags, resulting in insufficient decantation and eventually production losses in several metal producing industries. Experiments and previous simulations indicate that interfacial energies play an important role in this interaction.

In the present work, a recently developed phase field model is used to evaluate the influence of the morphology and fraction of the solid particles on the attachment behaviour of metallic droplets to solid particles.

When the metallic droplets wet the solid particle partly or fully, the size, shape and proximity of the solid particles influence the size and number of attached droplets. The perimeter per area only influences the amount of attached metal at high wettability. Moreover, the space available around the particle, determined by the shape and proximity of other particles, can restrict the amount of attached metal. The simulations reveal that, in practice, fewer but larger solid particles close to each other would give rise to less attached metal and thus the chance for metal losses by mechanical entrainment decreases.

1. Introduction

Solid particles in liquid slags can have a detrimental effect on the phase separation between slag and metal phase due to mechanical entrainment of metallic droplets by these solid particles. This attachment is encountered in a variety of industries, such as Cu smelters [1] and Pb reduction melting furnaces [2]. To understand the fundamental nature of the interaction, experimental efforts were recently reported [3]. Possible disadvantages of an experimental approach may be that many experiments are needed to investigate the influence of all parameters and that it can be inconvenient to reveal the effect of one single parameter separately.

A recently developed phase field model [4], however, can help in the understanding of the attachment. The model describes the growth and evolution of liquid metal droplets by spinodal decomposition in a liquid with dispersed solid oxide particles. The first simulations showed that the interfacial energies play an important role, which is in accordance with the obtained experimental results [3]. In our previously reported modelling work, the influence of the interfacial energies and initial slag composition on the attachment

of metallic droplets to solid particles was investigated. This evaluation was performed as a function of time for four different regimes, namely no wettability of the metal on the particle, low wettability, high wettability and full wettability [4].

In this paper, the model is used to investigate the influence of the size, shape and number of solid particles on the behaviour of the liquid metal droplets. The different shapes of the particles in the simulations were inspired by experimental observations of mechanical entrainment of Cu-droplets in liquid slags [5]. In addition, the simulations will also be used to classify and interpret experimental observations of the attachment of metal droplets to solid particles in liquid oxides in the PbO–FeO–CaO–SiO$_2$–Cu$_2$O–ZnO–Al$_2$O$_3$ system [5].

The model is summarized in Section 2, the reader is referred to [4] for more information concerning this model. Section 3 introduces the numerical implementation and the simulation parameters. The results are presented and discussed in Section 4.

2. Model formulation

2.1. Variables

The microstructure of a hypothetical O–M system is described by a non-conserved phase-field variable ϕ, used to distinguish between solid ($\phi = 1$) and liquid ($\phi = 0$), and a conserved composition

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field x_M, i.e. the local molar fraction of the metallic element. The interface between the different phases is diffuse in phase field models: the variables continuously change from one bulk value to another bulk value over the interface. Due to these diffuse interfaces, the interfaces do not have to be tracked explicitly.

The system is assumed to have a constant temperature and pressure and the concentration of solute in the precipitate is fixed. The molar volume V_m is the same in both phases and does not depend on composition. Convection is not considered and the solid particles are assumed to be present before droplet formation.

2.2. Evolution equations

Both the evolution of the conserved and the non-conserved variables are governed by the minimization of the total Gibbs energy. The evolution of the conserved variable is governed by the following mass balance equation

$$\frac{\partial x_M}{\partial t} = \nabla \cdot \left[M \nabla \left[(1 - h(\phi)) f'_{Liquid}(x_M) + h(\phi) f'_{Solid}(x_M) - \kappa_{x_M} \nabla^2 x_M \right] \right] \tag{1}$$

The coefficient M $(\text{m}^5/(\text{J s}))$ is related to the interdiffusion coefficient D (m^2/s) of the liquid as $D = A_{Sp}M$. κ_{x_M} (J/m) is the gradient energy coefficient for the liquid–liquid interfaces.

The fourth order polynomial $f_{Liquid}(x_M) = \frac{A_{Sp}}{2}(x_M - x_{eq,LO})^2$ $(x_M - x_{eq,LM})^2$ represents the homogeneous part of the free energy of the liquid phase. With $x_{eq,LO}$ and $x_{eq,LM}$ the equilibrium compositions of the free energy curve of the liquid, in which spinodal decomposition takes place, as this free energy describes a miscibility gap between these two equilibrium compositions in this compositional region where $\frac{\partial^2 G}{\partial x_M^2} < 0$ [6,7]. Here, 'LO' refers to the oxidic liquid (slag) and 'LM' to the metallic liquid, respectively. A_{Sp} (J/m^3) is the slope of this free energy curve.

Analogously, $f_{Solid}(x_M) = \frac{A_S}{2}(x_M - x_S)^2$, represents the bulk contribution of the solid phase as a function of composition. Solid phases in oxide systems are often modelled with paraboloid Gibbs energies to provide a continuum model formulation of solids described as stoichiometric compounds in thermodynamic databases [8,9]. x_S and A_S (J/m^3) are model parameters that determine the position of the minimum and the steepness of the parabola describing the free energy curve of the solid. The interpolation function $h(\phi)$ has the form $h(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ and is frequently used in solid–liquid systems [7,10]. With $h(\phi = 1) = 1$ in the solid and $h(\phi = 0) = 0$ in the liquid.

The initial uniform supersaturation of the oxidic liquid is represented by x_i. To initiate spinodal decomposition, fluctuations are required, which is done by adding a random noise term, from a normal distribution with mean 0 and standard deviation 0.001, in every 100th time step.

The non-conserved phase field variable ϕ evolves according to the following equation [11]

$$\frac{\partial \phi}{\partial t} = -L \frac{\delta F}{\delta \phi} = -L \left[Wg'(\phi) + h'(\phi)(f_{Solid} - f_{Liquid}) - \kappa_\phi \nabla^2 \phi \right] \tag{2}$$

where W (J/m^3) is the depth of the double well function and κ_ϕ (J/m) the gradient energy coefficient for the solid–liquid interfaces. L is the kinetic coefficient related to the velocity at which atoms can hop over an interface.

2.3. Interface properties

Two different gradient terms are present in the total energy expression, because two types of interfaces are present: solid–liquid and liquid oxide–liquid metal. These gradient free energy terms are responsible for the diffuse character of the interfaces. The concept of 'thin-interface' phase field models is used: the interfacial width is used as a numerical parameter that can be modified for numerical reasons without affecting other system properties, such as interfacial energy, diffusion behaviour or bulk thermodynamic properties [7]. The width of these diffuse interfaces is defined based on the absolute value of the gradient of the variable profile at the middle of the diffuse interface, where the profile is the steepest.

Following the approach of Cahn and Hilliard [12], the expression of the interfacial energy (J/m^2) of the liquid–liquid interface $\gamma_{LO,LM}$ is:

$$\gamma_{LO,LM} = \frac{1}{6} \sqrt{\kappa_{x_M} A_{Sp}} (x_{eq,LM} - x_{eq,LO})^3 \tag{3}$$

The interfacial energies (J/m^2) of the solid–liquid can refer to either solid–liquid oxide interfaces or solid–liquid metal interfaces, with the respective interfacial energies $\gamma_{S,LO}$ or $\gamma_{S,LM}$. These interfacial energies are not necessarily equal, but are composed in the same way and consist of two contributions, which is especially noteworthy about the previously developed model:

$$\gamma_{S,LO} \text{ or } \gamma_{S,LM} = \frac{1}{3\sqrt{2}} \sqrt{W \kappa_\phi} + \gamma_{S,Lk}^{\nabla x_M} \tag{4}$$

with k = O or M, when the oxide or the metal liquid is involved, respectively. The first term arises following the approach of Allen and Cahn [11] and the second term originates from the fact that a solid–liquid interface does not only imply a change in the phase field variable ϕ, but also a variation in the compositional variable x_M between the two equilibrium values across the solid–liquid interface. This yields a non-zero gradient term for x_M. Because this contribution cannot be evaluated analytically, the following assumption was made: the composition dependence of the Gibbs energy across the interface is approximated by a spinodal function.

$$f_{approx}(x_M) = \frac{0.5(A_{sp} + A_s)}{2}(x_M - x_S)^2(x_M - x_{eq,Lk})^2 \tag{5}$$

This gives,

$$\gamma_{S,Lk}^{\nabla x_M} \approx \frac{1}{6}(|x_S - x_{eq,Lk}|)^3 \sqrt{\kappa_{x_M} 0.5(A_{sp} + A_s)} \tag{6}$$

This approximation was validated by measurement of the contact angles in previous simulations [4], and the observed values agreed well with the predicted values.

3. Simulation set-up

3.1. Constant parameters in this study

The same parameter values were used as in [4]. These parameters are linked with properties in the physical system and the values of these properties are chosen based on typical orders of magnitudes for these specific parameters. Several values and descriptions of the used parameters are listed in Table 1.

$\gamma_{LO,LM}$ should be of the order of N/m [13,14] and the interfaces should at least contain five grid points. This results in the parameter values mentioned in Table 1 and yields the following values of interfacial energy and interfacial widths throughout all simulations: $l_{LO,LM}$ = 8.0687 grid points (or 1.02 nm), $\gamma_{LO,LM}$ = 0.9030 N/m and $l_{S,LO} = l_{S,LM}$ = 7.9057 grid points (or 1 nm). M is chosen in such a way that the diffusion coefficient $D = 4 \; 10^{-11} \; \text{m}^2/\text{s}$.

3.2. Variable parameters in this study

The reference system has a system size of [256 256 1] grid points (or [32.38 32.38 0.13] nm), with a slag with initial supersat-