

**Phase field modelling of the attachment of metallic droplets to solid particles in liquid
slags: influence of interfacial energies and slag supersaturation**

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Abstract

Several pyrometallurgical industries encounter production losses due to the attachment of metallic droplets to solid particles in slags. Although scarce, due to experimental challenges, the available results indicate the importance of interfacial energies.

Simulations based on a phase field model potentially circumvent this lack of experimental data and allow a more systematic insight into the observed phenomenon.

In the present work, a phase field model for solid-liquid binary systems with spinodal decomposition in the liquid is implemented to simulate the metal droplet formation and growth in slags with non-reacting solid particles. The simulations allowed evaluating the influence of the interfacial energies and initial slag composition on the attachment of metallic droplets to solid particles 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.

Keywords

Phase field model; spinodal decomposition; interfacial energy; droplets; wetting

1 Introduction

Decantation frequently is the last step in pyrometallurgical processes, allowing separation of slag and matte/metal. However, a perfect phase separation is virtually impossible in practice and valuable metals are lost or reprocessing is required. Insufficient phase separation can originate from mechanical entrainment of metallic droplets, of which the attachment to solid particles in slags is one of the possible reasons, as illustrated in Figure 1 [1]. This attachment creates production losses in industrial Cu smelters [2,3], Pb reduction melting furnaces [4] but also in other industries [5]. To improve the phase separation, the fundamental mechanisms governing this phenomenon need to be identified.

Recently, experimental investigation on this interaction has been reported [6], but generally experimental data on this interaction are scarce. The first experiments pointed towards an important role of interfacial energies in this interaction. The attachment is also believed to be related with redox reactions between the metal, the slag and the solid particles [7,8]. Many experiments would be needed to investigate the influence of all parameters and, even though the microstructure and composition can be investigated, it would be very difficult to study the effect of each parameter individually because it is virtually impossible to keep the others constant. Hence, it is not straightforward to reveal the underlying chemical and physical phenomena with experiments. Modelling the interaction between the solid particles and metallic droplets would provide a neat solution for these practical issues.

The phase field method has already proved to be a very powerful and versatile modelling tool for microstructural evolution, e.g. during solidification [9,10], solid-state phase transformations [11] and solid-state sintering [12]. In this paper, a model is introduced that captures the basic processes involved in the formation, growth and evolution of liquid metal droplets in an oxide melt with dispersed solid oxide particles. The model allowed us to investigate the influence of the initial supersaturation of the liquid and of the interfacial tensions on the behaviour of the liquid metal droplets by computer simulations. The details of the model are presented in section 2. Section 3 introduces the numerical implementation and the simulation parameters. The simulations are presented and discussed in section 4.

2 Model formulation

2.1 Variables and free energy functional

This work aims to introduce a model that captures the important features of the droplet formation and growth. A hypothetical binary system O-M is considered and the microstructure is described by the following position- and time-dependent field variables: a non-conserved phase-field variable ϕ , used to distinguish between solid ($\phi=1$) and liquid ($\phi=0$), and a conserved composition field x_M , i.e. the local molar fraction of the metallic element. The position of the boundaries as a function of time is implicitly given by the field variables, i.e. the variables continuously change from one bulk value to another bulk value over the interface.

The microstructure evolution in an isothermal system at constant pressure is driven by minimization of the total Gibbs energy. It is assumed that the concentration of the solute in the precipitate is fixed and the molar volume V_m is the same in both phases and composition independent. Convection is not included and the solid particles are assumed to be present before droplet formation.

The total free energy F (J) of the system is formulated as:

$$F = \int [f_{S-L,interf}(\phi) + (1 - h(\phi))f_{Liquid}(x_M) + h(\phi)f_{Solid}(x_M) + f_{\nabla x_M}]dV \quad (1)$$

The first term only differs from 0 at the solid-liquid interfaces and is therefore the contribution of the interfacial energy for the solid-liquid interfaces and is written as

$$f_{S-L,interf}(\phi) = Wg(\phi) + \frac{\kappa_\phi}{2}(\nabla\phi)^2 \quad (2)$$

with W (J/m³) and κ_ϕ (J/m) model parameters. $g(\phi)$ is a double well function with minima at 0 and 1: $g(\phi) = \phi^2(1-\phi)^2$. W is proportional with the depth of the wells. The second term in (2) is a gradient free energy term and is responsible for the diffuse character of the interface between liquid and solid.

The Cahn-Hilliard Gibbs free energy of the liquid phase has a homogeneous part $f_{Liquid}(x_M)$, described by a fourth order polynomial

$$f_{Liquid}(x_M) = \frac{A_{Sp}}{2}(x_M - x_{eq,LO})^2(x_M - x_{eq,LM})^2 \quad (3)$$

And a gradient part $f_{\nabla x_M}$ responsible for the diffuse character of the interface between the two different liquid phases and is described by

$$f_{\nabla x_M} = \frac{\kappa_{x_M}}{2} (\nabla x_M)^2 \quad (4)$$

Where $x_{eq,LO}$ and $x_{eq,LM}$ are the two minima of the free energy curve. A_{Sp} (J/m³) can be used to adjust the solubilities of the two phases. $x_{eq,LO}$ and $x_{eq,LM}$ are the equilibrium compositions of the oxidic liquid (slag), indicated with the 'LO', and metallic liquid, indicated with the 'LM', respectively. The initial uniform supersaturation of the oxidic liquid is represented by x_i .

The bulk contribution of the solid phase as a function of composition, $f_{Solid}(x_M)$, is modelled with a parabolic function:

$$f_{Solid}(x_M) = \frac{A_S}{2} (x_M - x_S)^2 \quad (5)$$

x_S and A_S (J/m³) are model parameters that determine the position of the minimum and the slope of the parabola. The interpolation function $h(\phi)$ has the form $h(\phi) = \phi^3 (10 - 15\phi + 6\phi^2)$. With $h(\phi = 1) = 1$ in the solid and $h(\phi = 0) = 0$ in the liquid.

Following the approach of Cahn and Hilliard [13], it can be determined that the interfacial energy (J/m²) of the Liquid-Liquid interface $\gamma_{LO,LM}$ equals:

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

The width of the diffuse liquid-liquid interface is defined based on the absolute value of the gradient of the composition profile at the middle of the diffuse interface, where the profile is steepest.

$$l_{LO,LM} = \left| \frac{x_{eq,LM} - x_{eq,LO}}{\left. \frac{dx_M}{dn} \right|_{x_M=0.5(x_{eq,LM}+x_{eq,LO})}} \right| = 4 \sqrt{\frac{\kappa_{x_M}}{A_{Sp}}} \left| \frac{1}{x_{eq,LM} - x_{eq,LO}} \right| \quad (7)$$

where n is taken along the normal to the interface.

The interfacial energies (J/m²) 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,

$$\gamma_{S,LO} \text{ or } \gamma_{S,LM} = \frac{1}{3\sqrt{2}} \sqrt{W\kappa\phi} + \gamma_{S,Lk}^{\nabla x_M} \quad (8)$$

with $k = O$ or M , when the oxide or the metal liquid phase is involved, respectively. The first term originates from the double well function and the gradient term for ϕ (see equation (2)) following the approach of Allen and Cahn [14]. The second term originates from the fact that across the solid-liquid interface x_M varies between the two equilibrium values and consequently there also is a gradient in x_M . This contribution cannot be evaluated analytically. Assuming the composition dependence of the Gibbs energy across these interfaces can be approximated by a spinodal function

$$\frac{0.5(A_{Sp}+A_S)}{2} (x_M - x_S)^2 (x_M - x_{eq,Lk})^2 \quad (9)$$

the second term is approximated as

$$\gamma_{S,Lk}^{\nabla x_M} \approx \frac{1}{6} \sqrt{\kappa_{x_M} 0.5(A_{Sp} + A_S)} (|x_S - x_{eq,Lk}|)^3 \quad (10)$$

This approximation was validated by measurement of the contact angles (see Table 4 in results section 4.3). The width of the diffuse solid-liquid interfaces is defined based on the absolute value of the steepest gradient of the phase field profile along the interface.

$$l_{S,LO} = l_{S,LM} = \left| \frac{1}{\frac{d\phi}{dn}|_{\phi=0.5}} \right| = 2\sqrt{2} \sqrt{\frac{\kappa_{\phi}}{W}} \quad (11)$$

In contrast to the solid-liquid interfacial energies, $l_{S,LO}$ equals $l_{S,LM}$ because the phase field variable ϕ changes the same way over a solid – liquid oxide interface as over a solid – liquid metal.

In this model, the interfacial width is considered 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 ('thin interface' model). [15] It follows from equation (7) that multiplication of A_{Sp} and κ_{xM} with a same factor will not affect the liquid – liquid interfacial width. Due to equation (6), however, multiplying A_{Sp} and κ_{xM} with a same factor will adjust the liquid - liquid interfacial energy. A similar line of reasoning can be made for the solid-liquid interfaces with the parameters W and κ_{ϕ} .

2.2 Evolution equations

Microstructural evolution is driven by the minimization of the total Gibbs energy. The temporal and spatial evolution of the conserved field x_M is governed by the following mass balance equation

$$\frac{\partial x_M}{\partial t} = \nabla \cdot [M \nabla [(1 - h(\phi))f'_{Liquid}(x_M) + h(\phi)f'_{Solid}(x_M) - \kappa_{x_M} \nabla^2 x_M]] \quad (12)$$

The coefficient M ($\text{m}^5 / (\text{J s})$) relates to the interdiffusion coefficient D , as defined in Fick's law, $J_M = -D \nabla x_M$, of the liquid as $D = A_{sp} M$.

For every 100th time step, a random noise term from a normal distribution with mean 0 and standard deviation 0.001, was added to initiate spinodal decomposition.

The evolution of the non-conserved phase field variable ϕ [14] is governed by the equation

$$\frac{\partial \phi}{\partial t} = -L \frac{\delta F}{\delta \phi} = -L [W g'(\phi) + h'(\phi)(f_{Solid} - f_{Liquid}) - \kappa_\phi \nabla^2 \phi] \quad (13)$$

L is the kinetic coefficient related to the velocity at which atoms can hop over an interface.

3 Simulation set-up

3.1 Constant parameters

The values of the parameters in the evolution equations are linked with physical system properties, such as diffusion coefficients and interfacial energies. In this study, a model system is considered. For most parameters, a typical order of magnitude was chosen, but some compromises were needed to limit the computation time, as explained below for each parameter. The model parameters are listed in Table 1. Typical computation times on an Intel® Core™ i7-3610QM CPU @ 2.30GHz processor with 8Gb RAM ranged from 2h to 4h for a system size of [256 256 1] and a simulation time of 10^6 time steps and from 10h to 13h for a system size of [512 512 1] and a simulation time of 10^6 time steps.

This work focusses on some of the possible affecting parameters. Therefore, the obtained results are primarily of theoretical importance. One of the differences with industrial practice is found in the fact that the industrial metal fractions are of the order of 5%, whereas in this study fractions ranged from 10 to 31%. Moreover, the interfacial energy is also affected by system parameters such as temperature and chemical composition, which were considered constant in this study.

Figure 2 displays the free energy curves of the liquid and solid phases. To avoid compositional changes in the solid phase during the initial stage of the simulation, the free energy curve of the solid was made five times steeper than the curve of the liquid phase.

The initial saturation of the solution was chosen between the inflection points of the spinodal liquid curve (where $\frac{\partial^2 G}{\partial x_M^2} < 0$) [16], namely: $0.60 < x_i < 0.88$. The maximum of the curve lies at $x_M = 0.74$.

According to literature [17,18], $\gamma_{LO,LM}$ is of the order of 1 N/m. Furthermore, the interfaces should at least contain five grid points for a sufficient resolution of the diffuse transition at interfaces and to reproduce accurately the surface energies [19].

M is chosen in such a way that the diffusion coefficient $D = 4 \cdot 10^{-11} \text{ m}^2/\text{s}$. With the values mentioned in Table 1, the liquid-liquid interfacial energy and the interfacial widths possess the following values for all simulations: $l_{LO,LM} = 8.0687$ grid points, $\gamma_{LO,LM} = 0.9030 \text{ N/m}$ and $l_{S,LO} = 7.9057$ grid points for the interface between solid and liquid oxide and $l_{S,LM} = 7.9057$

grid points for the interface between solid and liquid metal. It is assumed that the particle does not transform. Therefore, a very small value of the kinetic coefficient L is chosen.

Experimentally observed dimensions [6] of solid particles in slags are of the order of μm .

In the simulations the particle size of a single large rectangular particle is taken as 100 by 50 grid points, corresponding to 12.65 by 6.32 μm . For a system size of 256 by 256 grid points, corresponding to 32.38 by 32.38 μm , the particle volume fraction is thus 0.0763. In reality, large variations are found (from 2-6 wt% [20] to 25 wt% [6]) for the particle volume fraction. The conditions of the slag production are mainly responsible for this variation.

3.2 Variable parameters in this study

The effects of the solid-liquid interfacial energies and initial slag composition were investigated in the present simulations. The reference simulation time is 10^6 time steps.

3.2.1 Effect of S/L interfacial energy

Since it is assumed that the solid does not react and its composition is constant, x_S can be used as a parameter to adapt the interfacial energy. The composition of the solid particle remains constant during a single simulation and determines the value of the solid-liquid interfacial energies, as shown by equations (8) and (10). Thus, for a given $\gamma_{LO,LM}$, this x_S -value will determine the contact angle. The different interfacial tensions determine whether or not wetting will occur, as described by Young's equation (14)

$$\gamma_{S,LO} = \gamma_{S,LM} + \gamma_{LO,LM} \cos \theta \quad (14)$$

The effect of the x_S -value on the solid-liquid interfacial energies and the contact angle is demonstrated in Table 2. Non-wetting is expected for $x_S \leq 0.57$, a low wettability corresponding to $90^\circ \leq \theta \leq 180^\circ$ for x_S between 0.58 and 0.74, a high wettability corresponding to $0^\circ \leq \theta \leq 90^\circ$ for x_S between 0.74 and 0.90 and full wetting with a non-existing contact angle for x_S -values higher than 0.9.

3.2.2 Effect of initial supersaturation

Industrial metal fractions in slags after decantation are of the order of 5%. According to the lever rule, the minimal achievable value of the metal fraction in this model system is 0.211. Therefore, the x_I -values were kept minimal, but within the spinodal region.

Furthermore, for $x_I > 0.66$, metal strands are formed instead of droplets in the model system. The following three x_I -values were therefore considered: 0.61; 0.63 and 0.65.

According to the lever rule, the metal fractions are then 0.229, 0.271 and 0.312, respectively.

3.3 Initialisation

The solid particle within the supersaturated slag is initialised by setting the value of ϕ equal to 1 and x_M equal to x_S within a rectangle of 100 by 50 grid points and ϕ equal to 0 and x_M equal to x_i elsewhere. Initially, the phase field parameters display a sharp step at the solid-liquid interface, but they become diffuse during the first 1000 time steps of the simulation, where a larger value of L , $L_{initial}$, is used, to allow the interface to become diffuse (Table 1).

Due to the added noise, the metal droplets will form through spinodal decomposition of the supersaturated slag. Spinodal decomposition provides an easy way to initialize the metal droplet formation. Since it is not known whether the metal droplets in slags form through spinodal decomposition in reality, the physical interpretation of the simulations will be limited to the droplet growth. Moreover, the estimates for $\gamma_{S,LO}$ and $\gamma_{S,LM}$ only apply after decomposition of the liquid.

To verify the effect of droplet initialization, an alternative initialisation method was also investigated. This method consists of randomly positioning droplets with a radius chosen from a discrete uniform random distribution between 1 and 10 in the system until the proposed volume fraction of metallic droplets is reached or slightly exceeded. The droplets are immediately initialized with a composition of 0.98 and the slag in between with a composition of 0.50.

The results of a number of simulations with this type of initialisation can be found in section 4.4. The used metal volume fractions were 0.20 and 0.10, corresponding to x_I -values of 0.596 and 0.548, respectively, which are outside the spinodal region. The random noise term is not included in these simulations.

3.4 Numerical implementation

All data processing was performed using the commercial software package Matlab 7.12 (R2011a) [21]. The kinetic equations are solved numerically with the semi-implicit Fourier spectral method. [22] The benefits of this method are its implicit treatment of the laplacian, hereby eliminating the need of solving a large system of coupled equations, and

a better numerical stability, allowing larger time steps compared to the completely explicit treatment. Limitations of the method are the inherent periodic boundary conditions and the fact that the values of the gradient energy parameters and kinetic parameters have to be constant.

3.5 Post-processing

To quantify the results, the total metal fraction, the areas of metallic phase attached to a particle and the fraction of metallic phase attached to the particle were determined from the simulated microstructures as a function of time. The total metal fraction in the system is defined as the ratio between the total area of all droplets divided by the total area of supersaturated liquid:

$$f_{metal} = \frac{A_{metal}}{A_{matrix,t=0}} = \frac{A_{metal}}{A_{system} - A_{particle,t=0}} \quad (15)$$

Thus the area occupied by the particle at time step zero is subtracted from the total system size for the denominator in equation (15). A metal droplet is defined as the connected domain for which $0.71 < x_M - \phi x_S$ holds. This threshold provides values of metallic fractions closest to those predicted by the lever rule for several initial supersaturations as tested for systems without a particle after a long simulation time of $50 \cdot 10^6$ time steps (the difference between the actual and predicted fraction was 0.0007 for $x_i = 0.61$, 0.0001 for $x_i = 0.63$ and 0.0007 for $x_i = 0.65$). The predicted metal fraction used equilibrium values of the phases accounting for the Gibbs-Thomson effect (evaluated with a molar volume of $10^{-5} \text{ m}^3/\text{mol}$ at 1500K) [23,24]. It should be mentioned that the Gibbs-

Thomson effect with these parameters has only a limited influence on the equilibrium composition.

To investigate the attachment of the droplets to the solid particle, the droplet (defined as $0.71 < x_M - \phi x_S$) was enlarged with two grid point layers around the droplet and the particle (defined as $0.5 < \phi$) with three grid point layers. When these extended domains overlap, the droplets are considered to be ‘attached’. The total area of the attached droplets is determined as the number of grid points located within attached droplets and multiplied by Δx^2 . The fraction of attached metal is defined as the ratio of the total area of the attached droplets to the total area of metal droplets in the system (equation (16)).

$$f_{attached\ metal} = \frac{A_{attached\ metal}}{A_{metal\ total}} \quad (16)$$

Moreover, contour plots of $x_M - \phi x_S = 0.71$ were obtained at different time steps, to illustrate the microstructure evolution. Contact angles ($^\circ$) and contact lengths (pixel) were measured on contour plots at the final time step with the software program ImageJ [25].

4 Results and discussion

4.1 Accuracy

Several simulations (namely for $x_i = 0.63$; $x_S = 0.50$; 0.60 ; 0.70 ; 0.80 ; system size [256 256 1]) were performed four times to investigate the spread on the results. The average and standard deviation of the results at the last time step can be found in Table 3. Standard deviations for the fraction metallic phase were generally three orders of magnitude

smaller than the average value and those of the area and fraction attached metal are both at least one order of magnitude smaller than the average value.

One exception is the case of $x_S = 0.50$, for which the standard deviation is large. Moreover, it is, in fact, expected that the metal does not attach itself to the solid for this x_S -value.

The latter is indeed the case for three out of the four simulations, but in one simulation there are several sticking droplets, explaining the large standard deviation. An extension of the simulation time for this specific simulation showed that the droplets detach from the particle at a later time, indicating that the droplets were attached to the particle by coincidence. Despite the fact that this result clearly related to a statistical spread in the obtained results and the arbitrary choice of the simulation time, it was decided to include it with the other obtained simulation results. The particle probably hindered the droplets in their growth and therefore the droplets gave the impression to be attached.

The graphs in the results section display error bars corresponding to the abovementioned standard deviations. This value is only significant when wetting occurs. Thus, if wetting occurs, the maximum value of the standard deviation for every wetting regime was plotted.

Furthermore, at the considered time, the average amount of attached metal for $x_i = 0.63$ and $x_S = 0.70$ is lower than that for $x_i = 0.63$ and $x_S = 0.60$ for all simulations. For $x_S = 0.60$, the droplets are not attached to the particle from the start, but are attracted towards the particle. However, the amount of attached metal levels off once several droplets are attached to the particle. In contrast, for the case of $x_S = 0.70$, the droplets grow directly on

the sides of the particle and steadily grow, yielding a continuous increase in attached metal. After extension of the simulation time, the correct sequence (more attached metal for $x_S = 0.70$) was found. These observations indicate some statistical spread in the simulations and demonstrate the arbitrary nature of the simulation time chosen as 10^6 .

4.2 General observations

The different stages of spinodal decomposition near a solid particle with $x_S = 0.60$ in a system of size [512 512 1] with an initial supersaturation of $x_i = 0.63$ are illustrated in Figure 3. Figure 3a-g show $x_M - \phi x_S$ and the figures are scaled to the interval [0 1] in such a way that values lower/higher than the minimum/maximum value are converted to the minimum/maximum, respectively. Thus, the particle, defined as $0.5 < \phi$, appears as a black rectangle. Figure 3h shows a set of contour plots of $x_M - \phi x_S = 0.71$ (definition of metal droplets) at different time steps, to illustrate the evolution of the microstructure. The particle is displayed as a black rectangle. The legend corresponding to the different time steps represented in the contour plots is shown on the right of Figure 3h and will be the same throughout this study (the last time step is plotted with a bold black line).

We can distinguish three stages in the simulations. In the first stage, localized spinodal decomposition takes place near the particle, as is clear in Figure 3c-d. Secondly, non-localized decomposition takes place in the remaining supersaturated liquid. This is visible in the corners of Figure 3d. Finally, Ostwald ripening (the growth of larger droplets at the expense of smaller droplets, as indicated by the black arrows in Figure 3e and g) and

coalescence (the merge of two droplets, as indicated by the black circles in Figure 3 f) occur.

Figure 4 and Figure 5 illustrate the evolution of the metal fraction in the system and the area and fraction of metallic phase attached to the particle with time. This simulation was performed for $2 \cdot 10^6$ time steps. Similar trends were observed for the other simulations. Generally, the attached droplets were observed at various positions at the particle with several configurations, which also varied in time. As mentioned before, however, in this study we will mainly focus on the coarsening stage and will mostly compare the final values of the fraction of metal in the system found in the simulations after a certain simulation time (at which all considered systems are well within the coarsening regime).

4.3 Effect of the S-L interfacial energy and initial supersaturation

The effect of the solid-liquid interfacial energies was investigated by variation of the parameter χ_s , as explained in section 3.2.1 and illustrated in Table 2. The area occupied by the metallic droplets attached to the solid and the fraction of the metallic phase attached to the solid obtained in the simulations at time step 10^6 are shown in Figure 6 for initial slag compositions x_i -values of 0.61, 0.63 and 0.65.

Generally, a lower contact angle results in an increasing amount of attached metal. The discrepancy between the observed and expected trend for $x_i = 0.63$ ($\chi_s = 0.60$ and $\chi_s = 0.70$) was already discussed in section 4.1 and disappears when the simulation time is increased.

The initial supersaturation primarily affects the fraction of metallic phase present in the system. Higher initial supersaturations have more metal in the system and require a longer simulation time to let all the metal attach itself to the particle, causing a smaller fraction of attached metal. Moreover, if x_i increases, full wetting starts to take place at higher x_S -value (lower contact angle). This may seem as contra-intuitive because an increase in x_i results in a larger metal fraction in the system and thus in a larger chance of attachment to the solid particle. However, because more droplets are present in the system, the chance of growth (and thus Ostwald ripening) of a non-attached droplet also increases, unless the driving force for attachment to the particle (reflected in the interfacial energies and contact angle) is large enough, which is only the case for high wettability. Moreover, time may also play a role in the observation of full wetting. Figure 7 shows the evolution of the droplets and their attachment by means of contour plots of the droplets at different time steps.

In general, two features seem to influence the behaviour of the droplets: Ostwald ripening due to the Gibbs-Thomson effect and an effect due to the interfacial energies between the solid and the different liquids. Four different wetting behaviours are observed.

For non-wetting, non-existing θ or $\theta = 180^\circ$ ($x_S \leq 0.58$), Ostwald ripening has the largest influence. In this case, the $\gamma_{S,LO}$ value is much smaller than $\gamma_{S,LM}$ (Table 2). For this reason the liquid oxide is preferentially attached to the solid instead of the metallic liquid phase. Moreover, the absolute value of the difference between the two S/L interfacial energies is larger than 0.903, which is the value of $\gamma_{LO,LM}$. Resulting in a non-existing contact angle, i.e.

only liquid oxide is attached to the solid particle. The growth of the droplets seems to be restricted by the presence of the particle: first, the droplets gain a flattened shape and then the centre of the droplets shifts away from the particle to obtain a spherical shape while maintaining the preferential attachment of the oxide liquid instead of the metal.

At an initial supersaturation of $x_i = 0.63$, it seems (Figure 7) that the droplets start to stick to the particle and stay there. However, this observation should be treated with care (as discussed in Section 4.1). Note that the standard deviation on the measurements indicated a large uncertainty for $x_s = 0.50$ simulations.

For low wettability ($90^\circ \leq \theta \leq 180^\circ$, $x_s = 0.58-0.74$), the interfacial energy effect becomes larger and the droplets move towards the solid. Moreover, the absolute value of the difference between $\gamma_{S,LO}$ and $\gamma_{S,LM}$ becomes smaller than 0.903, but $\gamma_{S,LM}$ remains the larger value, which still favours the attachment of liquid oxide to the particle, but to a lesser extent. Thus, the solid particle is covered predominantly with liquid oxide and the metallic droplets cover only a small fraction of the particle's surface. The droplets either first grow next to the particle and eventually deflect to the particle (at $x_s = 0.60$ and as is especially clear for the case of $x_i = 0.61$) or nucleate immediately on the sides of the solid and either grow directly with metal provided by diffusion (at $x_i = 0.61$) or dissolve again due to Ostwald ripening of other droplets nucleated elsewhere in the system ($x_i = 0.65$). The former happens faster if x_i increases. The droplets are probably not immediately attached to the particle because the slag around the particle reaches a composition just above 0.50, corresponding to $\gamma_{S,LO} \approx 1.255$ and $\gamma_{LO,LM} \approx 0.744$. This combination of

interfacial energies yields, according to Young's equation, a non-existing contact angle.

This slag composition continuously changes, which provides a slow movement of the droplet towards the particle. This does not happen at higher initial supersaturations as the amount of metal is higher in such systems.

At high wettability, ($0^\circ \leq \theta \leq 90^\circ$, x_S values of 0.74 -0.90), the flat droplets grow immediately on the solid, coalesce there and eventually form a metallic layer surrounding the particle because the $\gamma_{S,LM}$ value becomes smaller than $\gamma_{S,LO}$ and thus the metallic liquid is preferentially attached to the solid. However, the absolute value of the difference between $\gamma_{S,LO}$ and $\gamma_{S,LM}$ remains smaller than 0.903, this results in partial wetting with the majority of the particle's surface being covered by the metal.

In the case of full wetting ($x_S > 0.90$), the absolute value of the difference between $\gamma_{S,LO}$ and $\gamma_{S,LM}$ is larger than 0.903 and $\gamma_{S,LO}$ is the larger one of the two. In this case, the metal forms as a layer on the solid, as opposed to the previous case, where initially the droplet shape can still be recognized.

The contact angles were measured and are listed in Table 4 together with the contact angles expected from Young's equation (14). In general, the agreement is good, showing that the approximation made in equations (8) and (10) is acceptable. The differences between the measured and the predicted angles can be attributed to measurement errors and also depend on the post-processing.

Apart from the angles, the contact length in Figure 7 was also measured in pixels as an indication of the wetting character. As a reference: the particle had a perimeter of 947

pixels. It should be noted that the droplet in the case of $x_i = 0.63$ and $x_s = 0.50$, had only a small contact area/length with the solid particle and probably did not represent a real attachment of the droplet to the particle, as an extension of the simulation time also showed that the droplets detached. Moreover, for $x_i = 0.61$ and $x_s = 0.74$ (not shown but behaviour is between $x_s = 0.70$ and $x_s = 0.80$ in Figure 7), first six droplets are present with each a contact angle of approximately 90° . These coalesce to two droplets with contact angles of 90° and finally one droplet is formed which encloses the particle, resulting in full wetting. This indicates that the simulation time also has an important influence.

In this work, the interaction between the solid particles and metallic droplets resulted from the interfacial energies between the solid, the liquid oxide and the liquid metal. It should also be mentioned that chemical reactions between the solid and the two liquid phases can take place and might affect the interaction, as shown by Villanueva et al. [26]. Therefore, future investigations will include additional parameters and phenomena such as the redox reactions occurring in the system under evaluation.

4.4 Effect of initialisation method

For the results discussed up till now, spinodal decomposition was used as a convenient way to introduce the metallic droplets in the system. To verify the effect of droplet initialization on the findings discussed in the previous section, results obtained with an alternative initialisation method, namely by randomly positioning droplets with a radius chosen from a discrete uniform random distribution in the system until the proposed volume fraction of metallic droplets is reached, can be found in Figure 8. The actual initial

metal fractions are 0.1009 ± 0.0005 for a proposed volume fraction of 0.10 and 0.2010 ± 0.0009 for a proposed volume fraction of 0.20.

Generally, the amount of attached metal is smaller in comparison with the simulations using spinodal decomposition, because the volume fractions are chosen to correspond to smaller x_i -values. However, the number of droplets is larger for this initialisation method. Nevertheless, again no favourable positions on the particle were observed for the droplets. Increasing the volume fraction of metal has a similar effect as an increase of x_i , as discussed in section 4.3. Furthermore, a decrease in the predicted contact angle results in increasing amounts of attached metal. In the low wettability regime, the droplet needs to be initialized close enough to the particle and should be large enough to be attached to the solid. If the droplet is not large enough, it will dissolve, even though it was initially attached to the particle. Larger droplets, when positioned nearby the solid, will move towards it. In comparison with the initialisation by spinodal decomposition, the alternative initialisation method yields more, but smaller droplets attached to the solid for low wettability.

In the high wettability regime, the size of the droplet has less influence on the final attachment as even intermediately sized droplets can be attached to the solid or can dissolve in favour of the formation of a metallic layer around the particle.

A disadvantage of the alternative initialisation method is that it is possible that all larger droplets are, by coincidence, concentrated in the border of the system, although the droplets are initialized randomly. The smaller droplets, situated around the particle, will

dissolve and no droplets are attached to the particle, even though this is favoured by the interfacial energies. As a consequence, a larger number of simulations are required to draw relevant conclusions than when the droplets form through spinodal decomposition, since the droplets are then first formed close to the particle. As we are interested in the interaction between the particles and the droplets, the spinodal decomposition is thus preferred as initialisation method as it allows obtaining the same conclusions in a more efficient way.

5 Conclusions

This study investigates the influence of the initial supersaturation of the liquid and the interfacial energies on the attachment of liquid metal droplets to solid particles in liquid slags by phase field simulations. In practice, when a fraction of the metallic phase is attached to the solid particles, this fraction cannot settle and the yield of the phase separation will decrease, which in turn means an important loss of valuable metals in several industries.

A phase field model for a two-phase solid-liquid system with spinodal decomposition in the liquid was implemented. It is assumed that the solid phase does not react.

In the simulations three stages were observed: first 'localized' spinodal decomposition takes place near the particle, then, the non-localized decomposition occurs in the remaining supersaturated liquid. Finally, Ostwald ripening and coalescence take place.

Depending on the interfacial energies, four regimes were observed: no wettability of the metal on the particle, low wettability, high wettability and full wetting. A higher initial

supersaturation generally resulted in a higher metal fraction in the system. The effect of the initial supersaturation on the fraction of attached metal was, however, not fully conclusive and also varied with time. The simulations show that the attached droplets do not have preferred positions, as various places with several configurations and variations in time were encountered.

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Figure 1 Experimental micrograph of Cu droplets attached to solid particles [1]

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Figure 6 Influence of x_s (and the corresponding contact angle and its cosine in the table underneath the left x-axis) on the area and the fraction of the metallic phase attached to the solid at $x_i=0.61$; 0.63 and 0.65

Figure 7 Contour plots of $x_M=0.71$ at different times in the simulations to illustrate the influence of the interfacial energies through the parameter x_s for values from 0.40 to 0.90 and of the initial supersaturation through the parameter x_i for values of 0.61, 0.63 and 0.65 on the attachment of the droplets to the particle

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