Calphad-based phase-field study of the interplay between spheroidal graphite growth and chemical segregation in ductile cast iron

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Abstract. Spheroidal graphite in ductile cast irons forms in a divorced eutectic solidification, controlled by interstitial diffusion of carbon through the enveloping austenitic shell. As technical cast irons are multicomponent alloys, carbon diffusion can strongly be affected by content and chemical gradient of other solute elements. During growth of a eutectic cell, all solute elements are partitioned at the austenite/liquid interface. Substitutional diffusion within the austenite is almost negligible, but expansion-induced spatial displacement of the iron-rich matrix and solute atoms during graphite growth significantly complicates multidimensional numerical simulation. A recently developed volumetric multi-phase-field approach, implemented in the Micress software, now accounts for the volume expansion and related matter and solute transport. In the present case study, this approach is applied to investigate the evolving chemical gradients and their potential effect on carbon diffusion during growth of a three-dimensional eutectic cast iron cell. Phase and concentration dependent thermodynamic data, partial molar volumes and diffusion coefficients are evaluated from linked Calphad-databases. The interface properties of the polycrystalline spheroidal graphite nodule are modelled based on a dedicated effective multi-faceted anisotropy function. A special target is to investigate whether increase in Si content may result in a significant reduction of the carbon flux, eventually favoring graphite degeneration and chunky growth.

1. Introduction
Microstructure evolution in ductile cast irons is challenging because of the complex interplay between interstitial and substitutional diffusion and the non-negligible role of volumetric expansion. The spheroidal graphite growth is mainly controlled by interstitial diffusion of carbon through the austenite shell. While being interstitially dissolved in austenite, the carbon atoms merely contribute to the material’s volume, but significantly increase in partial volume when transforming to graphite. As a consequence, the solidifying material locally expands in volume during graphite growth. This transition-related expansion can be exploited to counteract thermal shrinkage and minimize shrinkage porosity [1], but is also of importance for the kinetic control of the divorced eutectic transition. Despite their slow solid-state diffusion, the substitutional elements Si, Mn and Mg hardly exert a growth restricting effect on the austenite to graphite transition, because they are passively transported together with the displaced fcc-(Fe) matrix during local expansion [2]. Figure 1 illustrates the complex interplay between graphite growth, solute transport and expansion.
Figure 1. Scheme of the divorced eutectic growth of graphite. Carbon atoms diffuse from the liquid/austenite to the austenite/graphite interface driven by chemical gradients. The transition of the interstitial carbon atoms to graphite results in local volumetric expansion. Substitutional diffusion is of negligible importance and does not slow down the carbon-controlled transition, since the substitutional elements are passively transported together with the displaced fcc-(Fe) matrix.

Numerical 3D simulation of microstructure evolution has become feasible thanks to an extended volumetric multicomponent multiphase-field (Vol-MMPF) model [3, 4] which accounts for the changing partial molar volume of the individual elements and the related expansion-induced solute transport based on Calphad data. In a previous study [4], solute distribution maps were predicted for a hypoeutectic Fe-C-Si-Mg-Mn cast iron and validated against experimental as-cast data. The present study is based on the same approach, but aims at a better understanding of the interplay between spheroidal graphite growth and evolving chemical gradients during the divorced eutectic solidification. It has been suggested [5, 6] that chemical gradients of substitutional elements might essentially affect carbon transport by cross diffusion. Countering carbon cross diffusion fluxes were hypothesized to be a major reason for graphite degeneration. The here presented phase-field simulations shall serve as a basis to discuss the role of the initial Si concentration and related cross diffusion on the growth of a single three-dimensional eutectic cell from a slightly hypereutectic Fe-C-Si-Mn-Mg melt.

2. Microstructure simulations
Simulations were performed using the Vol-MMPF model [3] implemented in the Micress® software [7, 8] under assumption of two hypereutectic compositions with different Si content: (a) Fe - 3.8 C - 2.0 Si - 0.2 Mn - 0.045 Mg and (b) Fe - 3.8 C - 2.5 Si - 0.2 Mn - 0.045 Mg (all in wt%). All phase-specific thermodynamic, volumetric and diffusion data was evaluated from the databases TCFe8 [9] and MobFe3 [10] via the TQ interface of the ThermoCalc software [11] as illustrated in figure 2. The kinetic equations were corrected in the thin-interface limit [12], however without anti-trapping currents at the graphite/austenite interface, inconsistent with the volumetric approach. A dedicated finite-differences formulation [13] ensured high accuracy for a diffuse interface width of $1.6 \mu m = 4 \Delta x$. The side length of the cubic simulation domain with periodic boundary conditions was set to $40 \mu m$ (figure 3).
Figure 2. Illustration of the volumetric multicomponent multi-phase-field model (Vol-MMPF) [3, 4] and its implementation in the Micress® software. Phase-specific thermodynamic, volumetric and diffusion data is evaluated from Calphad databases.

Figure 3. Phase-field simulations of the divorced growth of a single eutectic cell in comparison for two hypereutectic cast iron alloys with different initial Si contents (a) 2.0% and (b) 2.5%. Both simulations were started at a temperature of 1266.85 °C and cooled by a constant heat extraction rate $\dot{q} = 7 \times 10^6$ Js$^{-1}$m$^{-3}$ (White: liquid, yellow: austenite, violet: graphite).
Both simulations started at a temperature of 1266.85 °C. The temperature was computed homogeneously throughout the simulation domain from the balance between growth related latent heat release and constant heat extraction \( (\dot{q} = 7 \times 10^6 \text{Js}^{-1}\text{m}^{-3}) \), resulting in a solidification time of approximately 300s. Figure 4 shows the predicted temperature and phase fractions in comparison for both alloys. Due to the effect of Si on the heat capacity, small temperature differences can be observed even before nucleation. Graphite nucleation was modelled with a critical undercooling \( \Delta T = 2 ^\circ C \) in the center of the domain. In alloy (a), this undercooling was reached after 70s at a temperature of \( T = 1170 ^\circ C \), in (b) already after 35.25 s at a significantly higher temperature of \( T = 1218.25 ^\circ C \). Austenite nucleation was modelled with a critical undercooling \( \Delta T = 3 ^\circ C \) in the melt with some distance to the graphite interface. This undercooling was reached almost at the same time for both alloys: (a) after 77.4 s at a temperature of \( T = 1160.15 ^\circ C \) and (b) after 78.7 s at a temperature of \( T = 1163.15 ^\circ C \).

Interfacial energies were modelled based on estimated data from literature [14, 15] under assumption of a weak cubic anisotropy for austenite and an effective multi-faceted anisotropy for the multi-crystalline graphite [4]. Table 1 summarizes the data specified for the individual interfaces. The assumed high interfacial mobility of the liquid/austenite ensures complete diffusion-control, whereas the lower mobility of the graphite interface was defined at the limit between diffusion- and interfacial-control. This limit is defined by the constraint that a further increase of the mobility value hardly affects the simulation results, while a reduction results in kinetic undercooling of graphite. It may be noteworthy that a reduced austenite/graphite mobility was found to trigger coupled eutectic growth (liquid→austenite + graphite) and multidimensional branching, proceeding at a higher temperature than the divorced eutectic growth (liquid→austenite, austenite→graphite), obtained in the here investigated diffusion-controlled limit.

| interface                  | anisotropic interfacial energy | anisotropic interfacial mobility |
|----------------------------|--------------------------------|---------------------------------|
| liquid/austenite           | 0.17 Jm\(^{-2}\)(mean)        | \(10^{-3}\)m\(^{3}\)J\(^{-1}\)(mean) | 0.05 (anisotropy) |
| liquid/graphite            | 1.46 Jm\(^{-2}\)(facet)       | \(3 \times 10^{-14}\)m\(^{3}\)J\(^{-1}\)(facet) | 5 \times 10^{-15}\)m\(^{3}\)J\(^{-1}\)(edge) |
| austenite/graphite         | 1.21 Jm\(^{-2}\)(facet)       | \(3 \times 10^{-15}\)m\(^{3}\)J\(^{-1}\)(facet) | 5 \times 10^{-15}\)m\(^{3}\)J\(^{-1}\)(edge) |

Figure 3 shows the evolving eutectic cell at \( t = 80 \) s, 85 s, 100 s and 150 s for both alloys. The most striking difference is that the size of the graphite nodule before encapsulation by austenite is much higher for alloy (b) than for alloy (a). At \( t = 100 \) s, the eutectic cells of both alloys exhibit a spheroidal geometry of comparable size. Although the whole solidification lasted about 300 s, only the first 150 s were evaluated in order to avoid artifacts from the cubic shape of the box and impingement of the eutectic cell. The molar fraction of solid at \( t = 150 \) s was approx. \( f_i = 0.3 \) for both alloys with the ratio between austenite and graphite being slightly higher for alloy (a) \( f_ia/f_ig = 11.03 \) then for alloy (b) \( f_ia/f_ig = 9.16 \). The corresponding intrinsic volume expansion, resulting from the balance between transition-related expansion and thermal shrinkage without consideration of melt feeding or pore formation, was (a) \( V/V_0 = 0.983 \) and (b) \( V/V_0 = 0.982 \). The ratio between austenite and graphite volumes was (a) \( V_a/V_G = 14.29 \) and (b) \( V_a/V_G = 11.83 \), corresponding to mean radii ratios of (a) \( r_a/r_G = 2.48 \) and (b) \( r_a/r_G = 2.34 \).

The major difference in the divorced eutectic growth of the two alloys is that alloy (b) solidifies at a higher temperature and also shows a slightly different recasenlence behavior (figure 4). Despite this difference, the graphite morphology of both alloys is very similar, except for some surface perturbations inherited from the moment of encapsulation. This difference can be explained by the fact that the austenite exhibited a smooth, stable front when covering the graphite surface in alloy (a), but formed some kind of surface dendrites in alloy (b) and as a consequence, the shell did not close in a single, but in several spots. This detail is here hardly visible, but was found to be more pronounced for further increased Si contents. It is still unclear whether the observed instability of the evolving three-phase-line can be explained by the larger nodule size only, or whether it is additionally affected by the increased Si segregation.
3. Chemical segregation

During the growth of the eutectic cell, the solute elements are partitioned at the phase interfaces and redistributed by diffusion and expansion-induced transport. Graphite was modelled with 100% carbon content and zero solubility for other elements. Figure 5 shows the evolution of the average contents of C, Si, Mn and Mg in the melt evaluated as function of time. Primary growth of graphite was found to reduce the carbon content, but hardly affect the Si, Mn and Mg content. After nucleation of austenite, the melt becomes enriched in Mn and Mg and depleted in Si. The C content of the melt rapidly increases during encapsulation of graphite, but temporarily decreases, before going up again. This change is less accentuated for alloy (b), where the carbon content continuously increases during encapsulation and subsequent divorced growth. Furthermore, the increased Si content of alloy (b) slightly reduces the enrichment in Mn, but increases the enrichment in Mg. The Si content itself seems to be simply constantly shifted by 0.5%.

The line profiles in figure 6, evaluated in horizontal direction through the center of the simulation domain, illustrate the spatial solute distribution at three moments in time (t = 80 s, 100 s and 150 s). In the liquid regions, all solute concentrations appear homogenous. The fact that the three-phase-line becomes morphologically unstable in alloy (b) provides some evidence that the growth of austenite from liquid might be limited by diffusional transport of Si, Mn or Mg in the melt, but this is not visible on the scale of the depicted solute profiles. In contrast, the chemical gradients in austenite, representing the driving forces for diffusion from liquid to graphite, are clearly visible. They are caused by the difference in composition between the austenite/graphite interface on the one side and the austenite/liquid interface on the other side. The corresponding solute partitioning was evaluated from the thermodynamic database [9] based on quasi-equilibrium calculations [8], comprehensively accounting for thermal, solutal, curvature and kinetic undercooling. It is important to note, that the quasi-equilibrium concentrations of the individual elements are not independent of each other. Figure 6 shows that the higher initial Si content of alloy (b) affects the profiles of all elements, with Si and Mn contents in austenite being increased and C and Mg being decreased.

Apart from their effect on the thermodynamic quasi-equilibrium conditions, the substitutional elements affect the carbon flux by cross-diffusion. In agreement with previous findings [4], the profiles of substitutional elements in austenite exhibit Scheil-type progression with negative gradients of Si and positive gradients of Mn and Mg in normal direction to the austenite/graphite interface. These gradients represent additional driving forces for the carbon flux, which was explicitly considered in the phase-field simulations based on chemical mobility data from the multicomponent database [9]. Especially the cross-diffusional contribution of the Si gradients to the carbon flux was found to be non-negligible, with an off-diagonal coefficient approximately half the size of the diagonal carbon diffusion coefficient and chemical gradients of the same order of magnitude. It is important to note that the impact of the negative Si gradient on the carbon diffusion flux counteracts the impact of the positive carbon gradient.

It has been supposed that an increased content of negatively segregating elements, such as Ni or Si, increases the negative chemical gradients and the related counteracting cross diffusion [5, 6], which might then result in an essential reduction of the carbon diffusion flux. However, this was not observed in the present simulations. Figure 6 reveals that the carbon and silicon profiles in austenite are significantly affected by the increased initial Si-content, but the corresponding change in chemical gradients is hardly visible. Moreover, a detailed evaluation revealed that any increase in the chemical gradient of Si is related to a simultaneous increase in C gradient, such that the resulting changes in carbon diffusion flux directly compensate each other. Hence, the diffusion fluxes and the transition kinetics remain almost unaffected by the increased initial Si content, while the thermodynamic conditions, i.e. the temperature and interface composition during the divorced eutectic transformation are significantly changed. Whether this may favour repeated nucleation of graphite in the melt and/or trigger transition to chunky growth at a critical Si content is still unclear and shall be the subject of future studies. In this context, it may also be of interest to compare alloys with different Si and C contents, but equal carbon equivalent.
**Figure 4.** Temperature evolution and phase fractions evaluated as function of time from two simulations with different initial Si contents.

**Figure 5.** Average contents of carbon, silicon, manganese and magnesium in the melt evaluated as function of time from two simulations with different initial Si contents.
Figure 6. Horizontal line profiles of carbon, silicon, manganese and magnesium evaluated at three different times $t=80\,\text{s}$, $100\,\text{s}$ and $150\,\text{s}$ from two simulations with different initial Si contents.
4. Conclusions

The interplay between spheroidal graphite growth and chemical segregation during the solidification of a single eutectic cast iron cell was simulated using a volumetric multi-phase-field approach. Thermodynamic and diffusion data, as well as element and phase specific partial molar volumes of the multicomponent Fe-C-Si-Mn-Mg alloy were evaluated from Calphad databases. As expected Mn and Mg segregated positively and Si negatively into the melt, while carbon segregation changes from negative to positive after encapsulation of the graphite by austenite. Carbon diffusion through the austenite shell was found to be mainly driven by the positive chemical gradient of C and the negative gradient of Si. The counteracting contribution of the silicon gradient to the carbon flux was found to be non-negligible, approximately of half the size of the contribution of the carbon gradient.

However, against previous expectations, no reduction of the carbon flux was observed when increasing the initial Si content from 2.0 to 2.5 wt%. The predicted carbon and silicon profiles in austenite were considerably shifted, but the observed change in chemical gradients was rather small. Moreover, any change in Si gradient was found to be directly compensated by a simultaneous change in C gradient. While the increased initial Si content hardly affected the diffusion flux, it essentially changed the nucleation and thermodynamic conditions. Graphite nucleated much earlier, which favored the primary growth of graphite from the melt and affected not only the graphite size, but also the morphology of the three-phase-line during encapsulation by austenite. Furthermore, the temperature and the interface compositions during the divorced eutectic were significantly changed. These effects are expected to be more pronounced for further increased Si contents. An interesting future task will be to investigate whether the modification of the nucleation and thermodynamic conditions or rather a simultaneous modification of the interfacial properties can explain the often reported impact of the initial solute concentrations on graphite degeneration.

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