The effect of alloy elements on the density variation of steel melt at the interdendritic region during solidification

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Abstract. Alloying elements in steels have essential effects on the formation of macrosegregation by inducing a density difference between the mushy zone and the bulk melt, and even by the alteration of the solidified microstructure. Hence, in terms of the thermodynamic laws for solidification of an idealized dilute solution, a systematic theoretical analysis on the effect of elements on the density variation of the interdendritic melt is presented for common Fe-based binary alloys. It shows that density variation closely associates with three crucial parameters: the microsegregation parameter $\lambda$, the temp-comp-expansion parameter $\beta$ and the initial composition $C_L^o$. With these derived parameters, a simple analytical model is proposed to assess the influence of alloy elements on density change. The theoretical analysis indicates that compared to silicon, the effect of carbon on the density variation cannot be ignored, which is remarkably different from the previous recognition of these two elements. The macrosegregation induced by carbon only is experimentally validated by two dissected 500 kg ingots with different carbon contents. Furthermore, to directly validate the results of theoretical analysis a macrosegregation model with two different microsegregation laws (lever rule and Scheil equation) is established. Then simulations of the convection during solidification in the experimental 500 kg reference ingot are performed for Fe-C and Fe-Si alloys, respectively. It demonstrates that numerically simulated effects of carbon and silicon on the interdendritic convection induced by density inversion are fairly consistent with the analytical predictions.

1. Introduction

Macrosegregation of solute elements in steels is usually a serious inhomogeneity problem impairing the quality of final products. Since the mid-1960s, huge amounts of research has been performed on the formation mechanism of macrosegregation [1-6]. It has been well recognized that the composition of an alloy often plays an essential role in macrosegregation formation by changing the dendrite morphology and magnifying the density variation of liquid melt in the mushy zone, which leads to intense interdendritic flow and finally results in the macrosegregation of elements in a solidified product. Specifically, reducing the content of Si and increasing the content of Mo [6] has been employed frequently as an effective approach to reduce channel segregates in steel ingots.
However, evaluating the density change or the convection intensity in the mushy zone from experimental results is difficult since the thermal and solute fields during experiments may not be accurately known. Commercial software packages, such as JMatPro, Thermo-Calc, ProCAST and Magma, are able to deliver some parameters in steels, but outputs from them are limited in their current calculations [7]. In addition, it has been evidenced by some previous reports [8-9] that in carbon steels, silicon has the most important influence on the change of liquid density, whereas carbon plays a negligible role. Nevertheless, experimental investigations on the macrosegregation in steel ingots have demonstrated that more serious segregation exists in high carbon steels compared with that in low carbon steels, which indicates that the effect of carbon content on the macrosegregation formation should not be neglected. Therefore, in order to clearly understand the influence of alloying elements on the formation of macrosegregation in steels, further research oriented on the relationship between alloying elements and the density difference is described in the current paper. Firstly, a theoretical analysis of the effect of alloying elements on the density change is carried out. Then two experimental steel ingots are dissected to verify the analytical results. Finally, the flow fields in the Fe-C and Fe-Si systems induced only by density difference during solidification of the 500 kg reference ingot are simulated numerically based on our theoretical analysis.

2. Theoretical analysis
Based on microsegregation models of the lever rule and the Scheil equation, for a dilute multicomponent steel melt the density change can be expressed as following [8],

\[ \Delta \rho = \sum_{i,j} \lambda_{ij} (c_i - c_j) \left( \frac{\Delta H_i}{10} \right) \]

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where \( \beta_i \) and \( \beta_j \) represent the density expansion caused by temperature and composition simultaneously for substitutional element \( i \) and interstitial element \( j \), respectively, and they are defined as the “temp-comp-expansion parameter”. \( \lambda \) is defined as the “microsegregation parameter” and is determined by microsegregation law. Then, the effect of elements on the density in the mushy zone via the initial concentration \( C_{L0} \), expansion parameter \( \beta \) and microsegregation parameter \( \lambda \), will be discussed in the following.

### 2.1. Temp-comp-expansion parameter \( \beta \)

In the derived temp-comp-expansion parameter \( \beta \), the values of \( \beta^o \) are almost the same in most of the published papers for various alloying elements and the value of \( \beta^o_{\rho} \) of iron can be obtained using the commercial software, such as the Thermo-Calc software. Therefore, the only controversial parameter is the liquidus slope \( m \) for each alloying element, which can be derived within the thermodynamic laws for a dilute solution. According to the dilute solution approximation, if both the solid and liquid conform to Raoult’s law, the relation between the concentration of an alloying element and the melting point of iron \( T_m (1809 \text{ K}) \) can be written as

\[

\ln \frac{w^L_i}{w^S_i} = \frac{\Delta_{fus}H_m}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right)

\]

where \( w^L_i \) and \( w^S_i \) are the mole fractions of solvent in the liquid and solid respectively (subscript: l solvent, s-solute); the molar enthalpy of fusion \( \Delta_{fus}H_m \) of iron is equal to 15490 J mol\(^{-1}\); \( R \) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)). As the concentration of alloy element is small and \( w^L_i = 1 - w^S_i \), \( w^S_i = 1 - w^L_i \), equation (2) can be approximated to:

\[

w^L_2 - w^S_2 = \frac{\Delta_{fus}H_m}{RT^2_m} (T_m - T)

\]

where \( w^S_2 = k \cdot w^L_2 \). Then for an element with atomic weight \( M \) the absolute value of the liquidus slope \( m \) can be obtained using equation (3), where the mole fraction of solute element has been changed to mass percentage,

\[

| m | = \frac{1000(1 - k)}{M}

\]

The calculated results of \( m \) using equation (4) for some common elements during phase transformation from liquid to \( \delta \)-iron or \( \gamma \)-iron, together with the previous calculation [8-11], are listed in table 1 for comparison. It denotes that the present calculated values for all the selected elements are rather close to the referred values.
Based on respective invoked parameters, table 2 shows the calculation results of $\beta$. Here, in our calculations $\beta^c = -0.635 \text{ kg m}^{-3} \text{ K}^{-1}$, which is obtained from Thermo-Calc software. The partition coefficients $k_i$ and $k_i^c$ are cited from Ref. [8], and are similar to that in Ref. [11]. It should be noticed that when we checked the values of $\beta$ as expressed by $\frac{\partial \rho}{\partial T} \frac{\partial T}{\partial C_i} + \frac{\partial \rho}{\partial C_i}$ in Ref. [8], the values listed in that paper are different from the calculated results using the corresponding input parameters. This is possibly because of a mistake in the units in the paper, which leads to the calculated values $\beta^c$ deviating two orders of magnitude from $\beta^c$. Thus we imposed these two sets of data together in table 2.

It shows that the obvious discrepancy between the present calculation and the previous reported results are the values of $\beta$ for C element. In the present calculation its value is in the same order of magnitude as those of Si, S and P elements, whereas, in both references, this value is so small that it can be ignored. This difference might be mostly ascribed to the different choices of $m$ and $\beta^c$ during the calculations of $\beta$. In the previous calculations the values of $m$ and $\beta^c$ referred to very early experimental data and varied with experimental methods and conditions. For example, the value of $\beta^c$ cited is different in some papers [8-9, 11], while in current calculations, it is obtained from Thermo-Calc software, which should be more reliable. For the calculation of C element, small differences of $m$ and $\beta^c$ will result in sensitive changes of $\beta$ because of the different signs between the product of them and $\beta^c$.

### Table 1. Comparisons between the calculated results of $m$ using the present model and references.

| Elements | C  | Si | Mn | P  | S  | Mo |
|----------|----|----|----|----|----|----|
| $m_{\beta}$, K (wt.%)$^1$ | -67 | -6.1 | -1.8 | -28 | -31 | -1.5 |
| $m_{\beta}^c$, K (wt.%)$^1$ | -58 | -18 | -4.5 | -30 | -30 | -4.2 |
| $m^{[8]}$, K (wt.%)$^1$ | -55 | -13 | -4.8 | -30 | -30 | -1.9 |
| $m^{[11]}$, K (wt.%)$^1$ | -76 | -10 | -4  | -31 | -34 | -3  |

$^1$Cited is different in some papers [8-9, 11], while in current calculations, it is obtained from Thermo-Calc software, which should be more reliable. For the calculation of C element, small differences of $m$ and $\beta^c$ will result in sensitive changes of $\beta$ because of the different signs between the product of them and $\beta^c$.

### Table 2. The calculated results of temp-comp-expansion parameter $\beta$ in different research.

| Elements | C | Si | Mn | P | S | Mo |
|----------|---|----|----|---|---|----|
| $\beta_a$, kg m$^{-3}$ (wt.%)$^1$ | -38 | -83 | -13 | -66 | -71 | 15 |
| $\beta_b$, kg m$^{-3}$ (wt.%)$^1$ | -43 | -76 | -11 | -65 | -71 | 17 |
| $\beta_c$, kg m$^{-3}$ (wt.%)$^1$ | -25 | -6800 | -700 | -4100 | -4700 | 1700 |
| $\beta_d$, kg m$^{-3}$ (wt.%)$^1$ | -0.25 | -68 | -7 | -41 | -47 | 17 |
| $\beta_e$, kg m$^{-3}$ (wt.%)$^1$ | -4 | -77 | -10 | -53 | -56 | 17 |

$^1$Current calculation results.

$^2$The results in Ref. [8].

$^3$The modified results from Ref. [8], and all the parameters are the same with the reference.

$^4$The results in Ref. [11].

2.2. Microsegregation parameter $\lambda$.

Furthermore, to precisely understand the effect of an alloying element on macrosegregation, the value of $\beta \lambda$ should actually be used rather than just $\beta$ according to equation (1). The calculated values of $\beta$ indicate that S and P will have strong effects on the density change, but their contents usually are limited within dozens of ppm during the steelmaking process. Hence, we will mainly focus on the effects of C and Si. Equations (5) and (6) show the calculated ratios of $\beta \lambda$ between carbon and silicon for $\delta$-iron and $\gamma$-iron respectively. It indicates that the values of $\beta \lambda$ of C and Si are rather close and so carbon will have a comparable effect on the density change to that of silicon, which is different from
the conclusions in Refs. [8] and [11].

\[
\left( \beta_C \cdot \lambda_C \right)_g / \left( \beta_S \cdot \lambda_S \right)_g \in (2.14, 2.56), f_L (0.05, 0.99)
\]  

\[
\left( \beta_S \cdot \lambda_S \right)_\gamma / \left( \beta_C \cdot \lambda_C \right)_\gamma \in (1.26, 3.08), f_L (0.05, 0.99)
\]  

![Figure 1](image)

**Figure 1.** The etched surfaces and carbon segregation ratio of two vacuum poured 500 kg ingots cut half along the axle plane. (a) High carbon (1.74 wt.%) ingot and its body dimensions; (b) low carbon (0.019 wt.%) ingot; (c) the segregation ratio of measured C concentration in the two ingots. The inset figure shows the positions of six drilled samples.

In addition, the current calculation results can also explain the noticeable phenomenon in the industrial process that macrosegregation of carbon in high carbon steels is more serious, relative to that in low carbon steels, as shown in figures 1(a) and (b). A sand mould was used for two round 500 kg ingots (other alloying element contents are the same for the produced ingots and are limited to a very low level during the refining process) and the sectioned surfaces were ground, polished and etched using a 20% HNO\textsubscript{3}-5% H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O solution. Six samples which were located in the same positions of each ingot were drilled for chemical analysis. Figure 1(a) indicates that in the high carbon steel both positive segregation (black region) at the upper part and the negative segregation at the bottom (white region) along the centreline are distinct, but in the low carbon steel (figure 1(b)) the segregation of carbon is not so obvious. Moreover, further measurements of carbon in the drilled samples (figure 1(c)) quantitatively show that the segregation ratio is generally larger in high carbon steel than that in low carbon steel. These compared results indicate that the effect of C element on the macrosegregation along the centreline in steel ingots should not be ignored and it will become more serious with increasing C content. These results are in accord once with the above theoretical analysis.

3. **Numerical implementations**

Furthermore, in order to elucidate the importance of carbon in driving natural convection and even macrosegregation, the flow field caused only by density inversion during solidification, neglecting solidification shrinkage and grain settlement, is simulated in binary Fe-0.36 wt.% C and Fe-0.36 wt.% Si systems respectively. The details of the applied model can be referred to our previous work [12], and here some key conservation equations are listed.
Conservation of mass:
\[ \nabla \cdot \langle \vec{U} \rangle = 0 \]  
(7)

Conservation of energy:
\[ \frac{\partial [\rho H]}{\partial t} + \nabla \cdot (\rho c_p \vec{U} T + \rho \vec{U} \Delta H) = \nabla \cdot (\alpha \nabla T) \]  
(8)

Conservation of solute:
\[ \frac{\partial [\rho C]}{\partial t} + \nabla \cdot (\rho \vec{U} C_L) = 0 \]  
(9)

Conservation of momentum (X direction):
\[ \frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho \vec{U} u) = -\frac{\partial P}{\partial x} - \frac{\mu_L}{K} u + \nabla \cdot (\mu_L \nabla u) \]  
(10)

Conservation of momentum (Y direction):
\[ \frac{\partial (\rho v)}{\partial t} + \nabla \cdot (\rho \vec{U} v) = -\frac{\partial P}{\partial y} - \frac{\mu_L}{K} v + \nabla \cdot (\mu_L \nabla v) + \rho g \left[ \beta_T \left( T - T_{ref} \right) + \beta_C \left( C_L - C_{ref} \right) \right] \]  
(11)

| Material/Property | \( \rho \) (kg m\(^{-3}\)) | \( C_p \) (J kg\(^{-1}\) K\(^{-1}\)) | \( \alpha \) (W m\(^{-1}\) K\(^{-1}\)) |
|-------------------|-----------------|----------------|----------------|
| Sand mould        | 1370            | 1070           | 0.73           |
| Insulation sleeve | 600             | 1130           | 0.9            |
| Covering flux     | 210             | 400            | 0.18           |
|                   |                 |                |                |
| Interfacial heat  |                 |                |                |
| transfer coefficient |              |                |                |
| Ingot and covering flux | 50       |                |                |
| Ingot and sand mould | 200            |                |                |
| Ingot and insulation sleeve | 50        |                |                |
| (W m\(^{-2}\) K\(^{-1}\)) | Coverage flux and the outside: \( 5 + 4 \times 5.67 \times 10^8 \times \varepsilon \times T^3, \varepsilon = 0.5 \) |
| Sand mould and the outside: \( 7.5 + 4 \times 5.67 \times 10^8 \times \varepsilon \times T^3, \varepsilon = 0.9 \) |

It should be noted that in the current model two different microsegregation models are applied: Lever and Scheil laws for C and Si respectively. As a reference, the experimental 500 kg ingot (see figure 1(a)) is numerically studied. The necessary boundary and initial conditions are also shown in table 3, and physical parameters of elements C and Si are referred to in the above analytical results. The other alloy properties such as density, specific heat, conductivity and secondary dendrite arm spacing and so on, are referred to in paper [13]. The grid size is 0.5 cm \times 0.5 cm. The initial superheat is set to zero.

4. Numerical simulation results and discussion
Figure 2 shows the velocity and solid fraction fields when the solidification front nearly reaches half of the ingots for Fe-0.36 wt.% C and Fe-0.36 wt.% Si alloys. It denotes that in both alloys the solutal buoyancy gradually overwhelms thermal buoyancy with the development of solidification, and the flow is ascending along the solidification front and descending along the centreline of the ingot. The convection finally dominated by solutal buoyancy can be well explained by the values of the temp-comp-expansion parameter \( \beta \) in table 2, which are negative and mean that \( |m \beta \alpha| < |\beta \alpha| \). In addition, it is worth noting that the mushy zone in the Fe-C system is wider than that in the Fe-Si system due to the larger liquidus slope induced by element carbon. Quantitatively, figure 3 shows that the average and maximum velocity magnitudes in the mushy zone where solid fraction varies from 0.15 to 0.45 are higher in the Fe-C alloy than those in the Fe-Si alloy, which indicates the prediction
by equation (5) that the driving force induced by density inversion in the Fe-C system is slightly larger compared with the Fe-Si system. Thus, the simulation results again demonstrate that the C element plays a comparable role on the evolution of thermosolutal convection in steels and are consistent with the theoretical analysis in section 2.

**Figure 2.** Predicted flow and solid fraction fields. (a) Fe-0.36 wt.% C; (b) Fe-0.36 wt.% Si.

**Figure 3.** The average and maximum values of velocity in the mushy zone of the two systems.

5. **Conclusions**
To summarize, the effect of alloying elements on the density change in the mushy zone in steel melts has been studied systematically by theoretical analysis, experiments and numerical simulations, and some main conclusions are yielded as follows:

1. A theoretical analysis with consideration of microsegregation parameter $\lambda$ and expansion parameter $\beta$ has been performed to assess the effect of elements on the density variation during solidification of steels. Guidance to composition design of steels can be offered to reduce the macrosegregation within this theoretical framework.

2. Theoretical analysis results have been verified by two dissected experimental ingots and the corresponding numerical simulations. They demonstrate that the effect of carbon on the density variation or even macrosegregation can be comparable with silicon, which is dramatically different from the previous recognition of these two elements that the contribution of carbon on the thermosolutal buoyancy can be neglected when compared to silicon.

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