INFLUENCE OF SEGREGATION PROCESSES ON SOLIDIFICATION TEMPERATURE OF STEELS

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Abstract
This paper deals with the possibility of prediction of solidification temperature of steel on the base of the description of (micro)segregation processes using selected microsegregation models. Two models of non-equilibrium crystallization are considered: the model with fully suppressed diffusion in the solid phase (Scheil’s model) and the model with partial diffusion in the solid phase (Brody-Flemings’ model). Original experimental data obtained from microanalytical measurements on samples of real steels were used for calculations and also the findings obtained at the modeling of microsegregation processes in steels. The results are compared with the solidus and liquidus temperatures calculated according to the relationships given in the available literature and with the liquidus and solidus temperatures obtained experimentally by DTA. Conclusions about the influence of microsegregation processes and influence of chemical composition on the solidification temperature of steels are stated.

Key words: Solidification temperature, microsegregation, solidus temperature, liquidus temperature.

1. INTRODUCTION
Solidification phenomena play a major role in such operations as casting, crystal growth and welding. Solidification proceeds at various rates, which are sometimes far from equilibrium. Thus, the microstructure obtained is generally not homogenous. Microsegregation is caused by redistribution of solute during solidification, as solute is generally injected into the liquid. Its fundamental cause is the difference between the thermodynamic equilibrium solubility of alloy elements in the different phases that coexist in the mushy region during solidification [1].

Dendritic structures are the most frequently formed microstructural morphologies of solidified alloys. Dendritic growth behavior is an important event during liquid-solid phase transformation, which intensively influences the subsequent solidification, and even determines the final structure and properties of the alloy. Different solidification temperature ranges may be responsible for the different solidification modes [2].

The purpose of the present work is to introduce simple methods for calculation and prediction of the temperature distribution during solidification, i.e. in the bounds of one “average” dendrite. In these methods, both the effect of solute segregation and the effect of multiple components are taken into account.

2. THEORETICAL BACKGROUND
Simple analytical mathematical models are often used for description of microsegregation behavior of a solute at the non-equilibrium crystallization. The heart of most simple microsegregation models is the assumed relationship between alloy concentration and solid fraction. The Scheil’s model [3,4] assumes the state with no diffusion in the solid phase, perfect mixing of a solute in a melt and directional solidification:
Brody and Flemings [5] have proposed a model that assumes complete diffusion in the liquid phase, incomplete back-diffusion in the solid phase and thermodynamic equilibrium at the solid-liquid interface:

\[ C_S = kC_0(1 - f_S)^{k-1} \]  

In the Eqs. (1) and (2): \( C_S \) is the solid concentration of a given solute element at the solid-liquid interface, \( C_0 \) is the initial liquid concentration, \( k \) is the equilibrium partition coefficient for that element, \( f_S \) is the solid fraction, and \( \alpha \) is the back-diffusion parameter (the Fourier number for a given solute element).

On the assumption of a straight liquidus line in the equilibrium phase diagram the dependence of the liquidus temperature \( T_L \) on a solute element concentration can be expressed as:

\[ T_L = T_M - mC_0 \]  

where \( T_M \) is the melting point of pure iron and \( m \) is the slope of the liquidus line of a solute element in the pseudobinary Fe-solute element phase diagram.

By combining Eqs. (1) and (3) and/or Eqs. (2) and (3) the relationship between the temperature and the solid fraction for the given solute element is given. This follows from the Scheil's model:

\[ T = T_M - (T_M - T_L)(1 - f_S)^{k-1} \]  

and this follows from the Brody-Flemings' model:

\[ T = T_M - (T_M - T_L)(1 - (1 - 2\alpha k)f_S)^{1-k} \]  

It follows from the Eqs. (4) and (5) that for \( f_S = 0 \rightarrow T = T_L \) and for \( f_S = 1 \rightarrow T = T_S \).

3. EXPERIMENT

The previously measured concentration data sets [6] were used for description of temperature distribution at dendritic crystallization. Concentration data were measured at the samples taken from the cross-section of a continuously cast steel billet. Chemical composition of steel in wt.% (only main elements): 0.806 C, 0.64 Mn, 0.20 Si, 0.011 P, 0.09 S. At each sample the concentrations in 100 points were measured along the line of 1000 µm long; altogether four elements were analyzed: carbon, manganese, silicon and phosphorus. A microanalytical complex JEOL JXA-8600/KEVEX Delta V – Sesame was used for microanalysis and the wave dispersing X-ray spectral method. Description of the experiment is given in [7] in detail. Concentration data sets measured in the sample A11 have been used for calculations in this paper, see Figs. 1 and 2.

Fig.1 Experimentally measured data  
Fig.2 Distribution curves of dendritic segregation
4. RESULTS AND THEIR DISCUSSION

Figure 3 presents the influence of the individual elements segregation on temperature distribution at solidification within the bounds of one "average" dendrite. That means from the core of the dendrite ($f_S = 0$) to the boundary between two adjacent dendrites ($f_S = 1$). The temperature distribution was calculated under the assumption that microsegregation of the given element during solidification could be described by the Scheil's model (Eq. (4), the dashed lines in the Fig.3) or by the Brody-Flemings' model (Eq. (5), the solid lines in the Fig.3). We can see from the Fig.3 that phosphorus shows the greatest influence on the decrease of temperature at the end of solidification, carbon has also great influence. Influence of manganese and silicon on decrease of the temperature in the course of solidification is not so big.

![Fig.3 Influence of the segregation of individual elements on the temperature distribution.](image1)

![Fig.4 Calculated temperature distribution within the bounds of one dendrite.](image2)

Figure 4 presents the calculated temperature distribution at solidification within the bounds of one "average" dendrite. The value of temperature for each solid fraction point was calculated as a weighted mean from the temperatures of individual elements (C, Mn, Si and P, Fig.3) for the same solid fraction point. We can see from Fig.4 that the assumption of no diffusion in the solid phase (Scheil's model) decreases the value of temperature at the end of solidification significantly more than the assumption of partial diffusion in the solid phase (Brody-Flemings' model). Two pairs of curves in Fig.4 differ in the liquidus temperature $T_L$ that is input into Eq. (4) and/or (5). The liquidus temperature was calculated according to the empirical relation given in [8] either from the heat composition (the higher values of the calculated temperatures in Fig.4) or from microanalytically measured concentrations of the four analyzed elements (the lower values of the calculated temperatures in Fig.4).

Summary of the calculated liquidus $T_L$ and solidus $T_S$ temperatures, it means the temperatures for $f_S \rightarrow 0$ ($T_L$) and for $f_S \rightarrow 1$ ($T_S$) in the Fig.4 is given in the first five columns of Table 1. In Table 1 these results are compared with temperatures calculated according to the empirical relations given in [8] and by commercial software IDS. Liquidus and solidus temperatures experimentally measured by DTA method at our department are also given in Table 1 (take notice of different chemical composition of investigated steel). It is obvious from Table 1 that our results are comparable with the results calculated (measured) by other methods. It follows from Table 1 and Fig.4 that the assumption of no diffusion in the solid phase (the Scheil's model) gives higher differences in the liquidus and solidus temperatures than the assumption of partial diffusion in the solid phase (the Brody-Flemings’ model). It is also evident from the first seven columns of Table 1 that the temperature differences between the liquidus and the solidus temperatures $\Delta T$ are higher for calculations taking into account the experimentally measured concentrations (sign "microanalysis" in Table 1). Calculations taking into account the heat composition show lower values (sign "heat" in Table 1).
Table 1 Temperatures $T_L$ and $T_S$ (in °C) calculated according to the Eqs. (4) and (5) for $f_S = 0$ ($T_L$) and $f_S = 1$ ($T_S$), according to the relations given in [8], by software IDS and experimentally measured by DTA-method.

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<td>126</td>
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*) Note to Tab.1: Chemical composition of the steel measured by DTA (in wt.%, main elements): 0.606 C, 0.39 Mn, 0.80 Si, 0.021 P, 0.006 S.

Calculation of temperature distribution according to the Eq. (4) or (5) requires knowledge of the partition coefficient $k$ and the back-diffusion parameter $\alpha$ for each element. In this paper the effective values of both parameters were determined by original mathematical models [9, 10] from experimentally measured concentration data sets given in Fig.2. It is not always possible to estimate the values of these parameters for all analyzed elements. In this case the so-called method of residual concentrations can be used.

The original method of residual concentration issues from the following assumptions: Experimentally measured concentration data are available for the given elements (e.g. data sets given in Fig.1). These data are then arranged in ascending or descending order (in dependence on the direction of segregation) and each number of measurements is transferred into the corresponding solid fraction (see Fig.2). Next assumption is that in steel, the solubility for most alloying elements is higher inside the melt than inside the forming solid. These elements are rejected from the solid phase during the solidification process and their content increases continuously in the liquid phase (the melt). Perfect mixing of a solute in a residual melt is further assumed. Under these assumptions it is possible to calculate the average concentration of the element in the residual melt, i.e. in the residual part of the curve in Fig.2 (for $f_S \epsilon (j, 1)$):

$$C_{R,j} = \left(\frac{1}{n-j+1}\right) \sum_{i=j}^{n} C_{S,i}$$  \hspace{1cm} (6)

where $n$ is the number of the measured points. The calculated residual concentrations of C, Mn, Si and P in the melt in dependence on the solid fraction are presented in Fig.5.

The temperature distribution during solidification can be then calculated from these residual concentrations according to the formula:

$$T_j = T_M - \sum_{i=1}^{n} m_i (C_{R,j})_i$$  \hspace{1cm} (7)

where $T_M$ is the melting point of pure iron, $m_i$ is the slope of the liquidus line of the element $i$ in the pseudobinary Fe-solute element phase diagram and $n$ is the number of analyzed elements. Calculated temperature distribution during solidification is given in Fig.6. In this case only four elements (C, Mn, Si and P) were taken into account because the measured concentration data sets were available only for these elements. The values of the parameter $m_i$ were adopted from the literature [8]. Boundary values of the calculated temperatures in Fig.6, i.e. for $f_S \rightarrow 0$ ($T_L$) and for $f_S \rightarrow 1$ ($T_S$), are given in the last column of Table 1.

We can see from Table 1 that the values calculated by the method of residual concentration are consistent with the values calculated from the microanalytically measured concentrations under the assumption of partial diffusion in the solid phase and (see column “Brody-Fl. (microanalysis)” in Table 1).
5. CONCLUSIONS

Influence of segregation processes on the temperature distribution during solidification has been studied in the presented paper. Two models of non-equilibrium crystallization have been considered for description of the microsegregation behavior of a solute: the model with no diffusion in the solid phase (the Scheil’s model) and the model with partial diffusion in the solid phase (the Brody-Flemings’ model). Original experimental concentration data sets of four elements (C, Mn, Si and P) measured on the sample of real steel have been used for calculation. Influence of segregation of individual elements on the temperature distribution at solidification within the bounds of one “average” dendrite has been determined for both assumptions – none and partial diffusion in the solid phase (Fig.3). Then the temperature distribution at solidification within the bounds of one “average” dendrite has been calculated (Fig.4), the effect of multiple components has been taken into account.

Furthermore, the original method of residual concentration has been developed. This method enables calculation of solute concentration in the residual melt at crystallization within the frame of one “average” dendrite. The residual concentrations of C, Mn, Si and P in the melt in dependence on the solid fraction have been calculated using the microanalytically measured data (Fig.5). Then the temperature distribution during solidification has been calculated from these residual concentrations (Fig.6).

It has been found out that: (i) phosphorus and carbon have the greatest influence on the decrease of temperature at the end of solidification, (ii) the assumption of no diffusion in the solid phase (the Scheil’s model) decreases the value of temperature at the end of solidification significantly more than the assumption of partial diffusion in the solid phase (the Brody-Flemings’ model), (iii) our results are comparable with the results calculated (measured) by other methods, (iv) the results calculated by the method of residual
concentration are consistent with the values calculated under the assumption of partial diffusion in the solid phase, (v) the results based on concentration data experimentally measured on a totally solidified sample include not only the process of crystallization and segregation but also the process of homogenization below the solidus temperature.

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REFERENCES


