OVERVIEW

Mathematical Analyses of Segregations and Chemical Compositional Changes of Nonmetallic Inclusions during Solidification of Steels[†]

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Reviewed in this paper are mathematical analyses for prediction of segregations and chemical compositions change of nonmetallic inclusions during solidification of steels. The studies conducted by the present author are used to construct the main stream of this article, and the author's view is delivered by introducing the related studies by other researchers and in comparisons among them.

In order to predict segregations of solutes during solidification of steels with more precision than previous microsegregation models such as Flemings-Brody equation and Clyne-Kurz equation, finite difference method was utilized to solve the Fick's law of solute diffusion in combination of thermodynamic equilibrium calculation at the solid/liquid interface. Stemming from the work, various attempts were conducted for its modifications, improvements and extensions of applicability. In order to control the chemical compositions of nonmetallic inclusions preferable to properties of steel products, mathematical analyses were done for the prediction of their chemical compositions change during solidification of steels. It utilized a microsegregation model by Clyne and Kurz and the assumption of equilibrium throughout the residual liquid including nonmetallic inclusions. In the most universal calculation method developed by the present author *et al.* simulation softwares developed in the field of calculation of phase diagram were fully utilized. An improved simulation method for solidification path analysis was introduced, which utilized a finite difference method to solve the solute diffusion between adjacent finite segments and equilibrium calculation in each finite segment to solve transformation.

The author's view for the future task in these field is summarized at the end. Development of mathematical models are highly promising, which consider macroscopic transport of solute and nonmetallic inclusions if necessary among the segments consisting the system interested and appropriate reaction models in each segment.

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I. Introduction

Since nonmetallic inclusions deteriorate the mechanical properties of steel products in many cases, many efforts have been paid for reducing their amounts by controlling the flows in tundish and casting mold to encourage the floatation and separation of nonmetallic inclusions. However, since it is impossible to remove all of the small inclusions, it is also important to control their chemical compositions and make them unarmful both during the production processing and as the quality of final products of steels.

In the case of anti-hydrogen-induced-cracking (HIC) steel as mentioned later, manganese sulfide (MnS) precipitations at spot-like segregations along the center line of continuously cast slabs act as crack initiation sites with elongated shape in the thickness center of line pipes

as final products. Therefore, sulfide shape control is aimed to prevent from MnS precipitation by addition of calcium⁽¹⁾⁻⁽³⁾. In the case of steel cords, since existence of hard nonmetallic inclusions cause breaking of wires during their drawing process, deoxidation conditions are adjusted to obtain nonmetallic inclusions with lower melting temperatures and better deformability⁽⁴⁾⁽⁵⁾. In addition, it is reconsidered recently to utilize nonmetallic inclusions positively for texture control⁽⁶⁾⁽⁷⁾, and it is necessary to control the inclusions which are effective for the aim. In these cases, since nonmetallic inclusions go through solidification of steels, their chemical compositions change and secondary precipitation are expected to occur through the reaction in the residual liquid steel of which chemical compositions change due to microsegregation of solutes. From this viewpoint, it is important to analyze the chemical compositions change of inclusions during solidification of steels.

On the other hand, since macrosegregation is formed by the movement of the residual liquid enriched by solutes in interdendritic region, and solidification of a

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macroscopically segregated region takes place with the little effect of liquid flow at the last stage of solidification, which can be analyzed in the same manner as for microsegregation, the analysis of microsegregation is also important from the viewpoint of macrosegregation analysis. In addition, although various countermeasures for prevention of macrosegregation are considered, microsegregation caused under the condition without any agitation cannot be avoided so easily. From this viewpoint, its analysis is further important. It is also important to analyze the above-mentioned chemical compositions change of inclusions during solidification. Therefore, the author would like to summarize and foresee the mathematical analyses in these field by the use of works conducted by the author *et al.* as the main stem of the present article.

II. Mathematical Analysis of Microsegregation during Solidification

Solute contents in the residual liquid C_L during solidification are given by a simple equations in the following cases:

- 1) in the case where whole system is in equilibrium;

$$C_L = C_0 / \{1 - (1 - k)f_s\} \quad (1)$$

- 2) in the case where complete mixing of solute in the liquid is assumed and solute diffusion in the solid is neglected;

$$(1 - k)C_L df_s = (1 - f_s) dC_L \quad (2)$$

- 3) and in the case where complete mixing in the liquid is assumed and solute diffusion in the solid is partially considered;

$$(1 - k)C_L df_s = \{1 - (1 - 2\alpha k)f_s\} dC_L \quad (3)$$

or

$$(1 - k)C_L df_s = \{1 - (1 - 2\Omega k)f_s\} dC_L \quad (4)$$

where f_s : fraction solid, C_0 : average solute concentration, k : solid-liquid partition coefficient, $\alpha = 4Dt_s/L^2$ (D : diffusion coefficient of solute in solid, t_s : local solidification time, L : dendrite arm spacing), and in the case 3) the solid-liquid interface with plain shape is assumed to advance in proportion to the square root of elapsed time. Equation (2) is the mass balance that the solute rejected at the solid-liquid interface due to the increase of fraction solid by df_s , $(1 - k)C_L df_s$, increases the solute content in the $(1 - f_s)$ of liquid by dC_L . Equation (3) is the mass balance that $2\alpha k f_s dC_L$ out of the solute rejected at the interface is consumed by diffusion into solid and the rest increases the solute content in the liquid. By adopting Ω instead of α eq. (3) is improved as eq. (4), which tends to eq. (1) when diffusion in the solid and α approach to infinity and Ω approaches to $1/2$, where Ω is defined by the following equation:

$$\Omega = \alpha \{1 - \exp(-1/\alpha)\} - 1/2 \exp(-1/2\alpha) \quad (5)$$

Equations (2) through (4) are integrated by the assumption of constant k throughout the solidification and the use of the relation $C_s = kC_L$, and eqs. (6) through (8) are derived.

$$C_s = kC_0(1 - f_s)^{k-1} \quad (6)$$

$$C_s = kC_0 \{1 - (1 - 2\alpha k)f_s\}^{(k-1)/(1-2\alpha k)} \quad (7)$$

$$C_s = kC_0 \{1 - (1 - 2\Omega k)f_s\}^{(k-1)/(1-2\Omega k)} \quad (8)$$

These are called the Scheil equation⁽⁸⁾ the Brody-Flemings equation⁽⁹⁾ and the Clyne-Kurz equation⁽¹⁰⁾, respectively. The following is found by the above equations: When α approaches zero, Ω approaches α , that is, eq. (8) approaches eq. (7) and eq. (7) approaches eq. (6). On the other hand, when α approaches infinity, Ω approaches $1/2$ and eq. (8) approaches eq. (1). Although these equations of microsegregation are lacking in preciseness, they are useful because of their simplicity if they are applied with an appropriate consideration. Among them, eq. (8) has wide applicability since it includes eqs. (1), (6) and (7). However, it has an ambiguity as to the rate at which Ω should approach $1/2$ when α approaches infinity. That is, the qualitative behavior of eq. (8) mentioned above does not change even if the following equation with any constant value of β is used instead of eq. (5):

$$\Omega = \alpha \{1 - \beta \exp(-1/\beta\alpha)\} - 1/2 \exp(-1/2\alpha) \quad (9)$$

In order to eliminate this ambiguity, the author *et al.* analyzed microsegregation by the use of the finite difference method (FDM)⁽¹¹⁾. The FDM has been widely utilized for the thermal analyses of solidification, but it has almost never been applied to the solute diffusion and distribution analyses in solidification which obey the same equation of transport. The rejection of excess solute, which is not distributed into solid in the solute distribution analysis looks similar to the release of the latent heat, which corresponds to the enthalpy difference between solid and liquid, in the thermal analysis at the solid-liquid interface according to its advancement. However, while the interface temperature and the amount of latent heat can be predetermined in the latter analysis, the amount of rejected solute can only be given during the analysis in the former analysis since the content of a solute at the interface is only given in the relation to the temperature and the contents of other solutes and the amount of the rejection depends on them. The former analysis seems to have some difficulty at this point in comparison with the latter analysis.

In any case, the advancement of the interface was analyzed by the use of FDM under the following conditions as shown in Figs. 1 and 2: 1) The history of the temperature at the region for the analysis T_A is given beforehand, and 2) the S/L interface is in local equilibrium. Practically, the interface was advanced by one element spacing instantaneously when the liquidus temperature T_L calculated by the solute contents in the N -th element, liquid element at the S/L interface, reaches T_A . The solute contents in the N -th and $(N+1)$ -th elements just after the interface advancement were calculated with the consideration that the total amount

Fig. 1 Model for transverse cross-section of dendrite (a) and portion for analysis selected from it (b)⁽¹¹⁾.

of each solute in these elements is conserved at the advancement and the ratio of solute content in the N -th element to that of the $(N+1)$ -th element is partition coefficient k after the advancement. Since the solute contents in the $(N+1)$ -th element naturally becomes very high due to this procedure, T_L calculated by these contents becomes much below than T_A . Therefore, the diffusion of the enriched solutes towards both solid and liquid was analyzed by the FDM in the next stage, while the location of the interface was fixed and the ratio of solute content in the N -th element to that in the $(N+1)$ -th element was kept as k , i.e., these elements were assumed to be in equilibrium. The solute contents in these elements decreases due to the diffusion as time elapsed and T_L calculated by the contents increases. Since T_A decreases as time elapsed, on the other hand, T_L becomes equal to T_A at some point. At this point the S/L interface was advanced by an element spacing again. By the repetition of these procedures, microsegregation can be analyzed while the S/L interface advances approximately satisfying $T_L = T_A$. The calculated microsegregation by this method for the cases in which the above mentioned simple equations for microsegregation can be applied agrees well with that predicted by those equations. In addition, it was demonstrated that this method can be used to predict the microsegregation and local solidification time measured in the unidirectional solidification experiments and the state of spot-like segregation observed in con-

(a) —: When $(N-1)$ -th element completes its solidification, —: When N -th element solidifies subsequently, (b) —: Actual temperature given, —: Liquidus temperature calculated from the solute contents in the liquid at the solid-liquid interface.

Fig. 2 Schematic view of solute distribution (a) and temperature changes (b)⁽¹¹⁾.

tinuously cast slabs with satisfactory agreement⁽¹¹⁾.

This method was improved by Ueshima *et al.*⁽¹²⁾ so that the δ/γ interface was considered as well as the S/L interface (Fig. 3), and effects of alloying elements on microsegregations in the systems with δ/γ transformation⁽¹³⁾. Kobayashi *et al.* proposed a method to eliminate the awkward stepwise motion of the S/L interface by adopting new variables in the solid defined by solute contents divided by partition coefficient k instead of contents themselves, which are continuous at the S/L and δ/γ interfaces⁽¹⁴⁾. Battle and Phelke calculated local solidification time and microsegregation of nickel during solidification of Fe-Ni alloys by simultaneous thermal and solute distribution analysis, in good agreement with the observations⁽¹⁵⁾. Wang *et al.* also analyzed microsegregation of stainless steels by the use of the one-dimensional FDM with a moving boundary, where the diffusion of nickel is assumed to be a rate control process of the δ/γ transformation and the solute contents at the δ/γ interface follows the δ/γ equilibrium concentrations corresponding the temperature history calculated in advance⁽¹⁶⁾. The calculated fraction of the residual δ was in good agreement with the observed results. Matsuda *et al.* modeled the solidification of two-phase stainless steel as follows: 1) Solutes in the liquid are completely mixed and the solute contents in the solid adjacent to the liquid

Fig. 3 Change in phosphorus distribution in dendrites. Cooling rate: 27°C/min. (a) 1498°C, (b) 1485°C and (c) 1333°C⁽¹²⁾.

changes keeping equilibrium with the liquid; and 2) the S/L interface advances stepwise by an element spacing in the same manner as the present author's method when T_L calculated by the C_L 's in the liquid reaches T_A ⁽¹⁷⁾. They solved two dimensional diffusion of solutes by the use of the 2D-FDM and advanced the S/L interfaces normal to the x and y -directions toward the x and y -directions by one element spacing, respectively. By this calculation, the two-dimensional solute distribution could be analyzed and the calculated results agreed well with the observation of two-dimensional segregation. In addition to these numerical analyses, Ohnaka proposed an improved equation for microsegregation by the use of an integral profile method⁽¹⁸⁾. He could reproduce the results of numerical calculation with less computational time (Fig. 4).

III. Mathematical Analysis of Chemical Compositions Change of Nonmetallic Inclusions

1. Coupled precipitation model

Mathematical analysis was done on the chemical compositions change of nonmetallic inclusions during solidification from the viewpoint mentioned in the introduction⁽¹⁹⁾. Nilles considered the amount of oxygen consumed by the MnO precipitation and subtracted them from the total amount of oxygen segregating in the residual liquid when he analyzed rimming action and calculated the dissolved oxygen in the liquid, long time ago⁽²⁰⁾. Many analyses were made to predict secondary precipitation based on the calculated solute contents and their multiplication regarding precipitation in the

residual liquid, as Stachura⁽²¹⁾ analyzed AlN precipitation in the interdendritic segregated region as an example. In addition, Miettinen mathematically analyzes the equilibrium precipitation of manganese sulfides in the liquid by solving the solute diffusion in the γ phase by the FDM assuming that solutes are completely mixed both in the liquid and δ phases⁽²²⁾. However, these analysis methods have not been developed so that as many precipitations as desired can be analyzed simultaneously. Then the present author analyzed how nonmetallic inclusions in the residual liquid change their compositions, what newly precipitates and what is redissolved with consideration of solidification segregation based on the assumptions similar to those utilized in the derivation of eqs. (7) and (8) (Fig. 5)⁽¹⁹⁾. That is, the followings are assumed: (1) Local equilibrium at the S/L interface, (2) complete mixing of solutes and homogeneous distribution of inclusions in the liquid, (3) applicability of Clyne-Kurz model to solute diffusion into the solid, (4) neglect of pushing-out of inclusions by the S/L interface, i.e., smooth transfer of inclusions into the solid in proportion to the increment of fraction solid, and (5) neglect of chemical reactions in the solid. The following equation was derived by the use of the above-mentioned assumptions:

$$(1 - k^i) dC_L^i df_s = \{1 - (1 - 2\Omega^i k^i) f_s\} dC_L^i + (1 - f_s) \times \sum_j R_{ij} dP_j \quad (10)$$

where superscripts indicate that the value is that of the solute i . Ω^i is the Ω value calculated by the use of D^i and

Fig. 4 Comparison of various equations for solute (Mn) concentration change in a Fe-1.52 mass%Mn alloy (a) and that of C in Fe-0.13 mass%C alloy (b)⁽¹⁸⁾.

Fig. 5 Schematic diagram for coupled precipitation model during solidification⁽¹⁹⁾.

α^j . P_j is mole fraction of component chemical compound j which exists in nonmetallic inclusions, and R_{ij} is the number of mole of solute i in one mole of component chemical compound j calculated based on stoichiometry of compound j . Equation (10) equals eq. (4) for micro-segregation when the last term is dropped. The last term corresponds to the amount of dissolved solute i consumed by the increase of compound j in the liquid. When dP_j is negative, the amount of the dissolved solute increases due to the dissolution of compound j . Equation (10) gives the relation between df_s and dC_L^i and its integration gives C_L^i as a function of f_s , if P_j 's are all zero. When one of P_j 's becomes a nonzero value, the unknown value dP_j is to be newly added, but also the equation of equilibrium for this precipitation is newly added by the use of assumption (2):

$$\prod_i a_i R_{ij} = K_j a_j \quad (11)$$

where, a_i : activity of solute i in the residual liquid, a_j : activity of the compound j in the inclusions and K_j : equilibrium constant for precipitation of the compound j calculated by the standard free energy of the formation of the compound j . a_i and a_j can be calculated as functions of C_L^i and P_j , respectively. Since K_j is a function of the temperature and the temperature is the liquidus temperature calculated by C_L^i based on the assumption (1), K_j is also a function of C_L^i . Therefore, the following equation derived from eq. (11) gives a new relationship between dC_L^i and dP_j :

$$\sum_i R_{ij} da_i / a_i = dK_j / K_j + da_j / a_j \quad (12)$$

Since the number of equations increases by the same amount as the number of unknown variables increases, dC_L^i 's and dP_j 's can be solved as functions of df_s by the combination of eqs. (12) and (10). By integration of them, the change of C_L^i 's and P_j 's are obtained at various f_s . Since various precipitation, its growth and dissolution due to equilibrium relation with segregating solutes in the residual liquid can be analyzed in a coupled manner by this model, the author would like to name it the coupled precipitation model.

In order to realize the sulfide shape control properly as a countermeasure for the prevention of hydrogen induced cracking in anti-HIC steel, a few parameters were proposed to obtain the appropriate balance among calcium and other chemical compositions⁽¹⁾⁻⁽³⁾. However, chemical compositions change of nonmetallic inclusions during solidification is not precisely considered in these parameters. This drawback was pointed out in the analysis conducted by Kitamura *et al.*⁽²³⁾ Therefore, the coupled precipitation model was applied to the analysis of chemical compositions change of inclusions during solidification of a spot-like segregation along the center line of continuously cast slabs of anti-HIC steel. The analyzed results are in the following paragraphs.

Spot-like segregations are considered to be formed by solidification of solute enriched liquid which is squeezed out of the interdendritic region of solidifying dendrites

with relatively high f_s due to solidification shrinkage and/or bulging and entrapped with spot-like shape at the center of slabs. When we analyzed the segregation, well agreements were obtained with the observed state of segregation in slabs in the case that we assumed that the interdendritic liquid of dendrite with $f_s=0.90$ was squeezed out and gathered. Therefore, we also utilized this understanding in the analysis of inclusions. Table 1 lists the average chemical compositions of steel analyzed and the solute contents in the residual liquid at $f_s=0.90$, C_L^{90} , in interdendritic region. This was calculated by the use of eq. (8) with $L=200\text{ }\mu\text{m}$ and $t_s=200\text{ s}$, which correspond to secondary arm spacing and local solidification time at the center of continuously cast slabs. The C_L^i 's and P_j 's were solved based on eq. (10) as functions of f_s when spot-likely segregated liquid with compositions of C_L^{90} solidified. In this case the radius of spot was used as L value and 200 s was used as t_s . Dissolved solute C, Si, Mn, P, S, Al, Ca and O and precipitation of CaO , Al_2O_3 , MnS and CaS were considered. The activities of CaO and Al_2O_3 , a_{CaO} and $a_{\text{Al}_2\text{O}_3}$, in $\text{CaO-Al}_2\text{O}_3$ binary were given as functions of their concentrations. The activities of MnS and CaS were given as unity when they precipitated. These manipulations regarding activities were much improved by the use of CALPHAD methods which are shown in the next section. The initiation of the precipitation of the compound j was detected at the point where the left hand side of eq. (11) calculated by C_L^i exceeded

Table 1 Chemical compositions of anti-HIC steel on average and in the residual liquid of growing dendrite at fraction solid of 0.9 (calculated value)⁽¹⁹⁾.

(%)	C	Si	Mn	P	S	Al	Ca	O
Average	0.081	0.16	1.02	0.0050	0.0012	0.0290	0.0033	0.0025
C_L^{90}	0.317	0.218	1.32	0.0203	0.0090	0.0447	0.0270	0.0270

C_L^{90} : Solute content in liquid phase at $f_s=0.9$ obtained by Clyne-Kurz equation. ($L=200\text{ }\mu\text{m}$, $t_s=200\text{ s}$).

the right hand side, and the annihilation of the precipitation of the compound j was detected at the point where P_j became equal to zero since the calculation was proceeded with eq. (11), i.e. eq. (12), satisfied as far as the compound j existed in the inclusions.

The calculated results are shown in Fig. 6 for $L=100\text{ }\mu\text{m}$. The amount of each oxide and sulfide is indicated as weight percent of oxygen and sulfur which exist as each oxide and sulfide, respectively. Based on the results, most oxygen is captured as $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (which is abbreviated as C_{12}A_7 and other compounds are also abbreviated similarly in the figure and the following text) and the amount of dissolved oxygen is less than 1 ppm at the beginning of the solidification of the spot-like segregation. Most calcium left after the formation of C_{12}A_7 is used to form CaS , and the amount of dissolved calcium is in the order of 0.01 ppm. Then, as solidifica-

Fig. 6 Changes of the amounts of dissolved solutes (a) and nonmetallic inclusions (b) in the residual liquid during solidification of a spot-like segregation with $L=100\text{ }\mu\text{m}$ (calculated values)⁽¹⁹⁾.

tion proceeds, CaO in the CaO–Al₂O₃ compound decomposes, where the decomposed Ca is used to capture segregating S as CaS and its amount increases, whereas the decomposed O is captured by dissolved Al and Al₂O₃ concentration in the CaO–Al₂O₃ compound increases. However, in this case, i.e. for $L=100\text{ }\mu\text{m}$, CaO does not completely decompose and the segregating S can be captured as CaS throughout the completion of solidification, which prevent MnS precipitation.

On the contrary, in the case of $L=1000\text{ }\mu\text{m}$ with the same chemical compositions as a initial condition, the calculated result indicates that CaO decomposes completely at $f_s=0.98$ and MnS begins to precipitate at the end of solidification since only the dissolved calcium is the calcium source to capture the segregating sulfur after the decomposition of CaO (Fig. 7), while the general tendency is quite the same as that in the case of $L=100\text{ }\mu\text{m}$. Dissolved Ca, S and O are calculated to increase sharply at the later stage of solidification as shown in Fig. 6(a), which is resulted from large negative values of interaction parameters $e_j^{(i)}$ among these elements in the dilute solution approximation. That is, they reduce their activity coefficients each other very much at this stage, and their activities are almost unchanged. Similar discussion was made already for Al₂O₃ precipitation⁽²⁴⁾. Careful attention must be paid to the composition range for the applicability of the dilute solution model. Otherwise, it is to be expected that CaS does not precipitate in the liquid with high Ca and S contents as an extreme case. In the case of Fig. 6, the calculated amounts and compositions

Fig. 7 Change of the amounts of nonmetallic inclusions in the residual liquid during solidification of a spot-like segregation with $L=1000\text{ }\mu\text{m}$ (calculated value)⁽¹⁹⁾.

of inclusions do not have much errors even if the calculation of the dissolved amounts of Ca, S and O contains errors, since their amounts are negligibly small.

The results obtained above are compared with the observation in actual slabs. Figure 8 shows the observed relation between fraction solid and fraction of each compound existing below the fraction solid, which was obtained by counting the accumulated number of each compound from the beginning of solidification done by Arihara *et al.*⁽²⁵⁾ They examined the sequence of the solidification of a spot-like segregation by the use of equi-concentration contours of Mn; that is, they considered that the higher the Mn concentration in a region, the later the region solidified. If a compound is distributed homogeneously over the spot-like segregation the accumulated number of the compound increases linearly to f_s , and the relation shown in Fig. 8 becomes a straight line with a gradient of 45°. However, the relation for CaO shows an upward convex curve, which means that CaO exists more in the earlier stage of the solidification than in the later stage. On the other hand, the relation for CaS shows a downward convex curve, which means that CaS exists more in the later stage of solidification. Further, it is shown that MnS exists only at the end of solidification. These observations all agree qualitatively well with the calculated results shown in Figs. 6 and 7. In addition, from other observations that CaS is enriched in the periphery of a inclusion⁽²³⁾⁽²⁶⁾, it can be concluded that CaS precipitates more in the later stage of solidification.

Fukuda *et al.* examined by observation the relationship between the diameter of a spot-like segregation and the maximum Mn concentration in the spot-like segregation, where the region with Mn concentration higher than 1.32 times of its average concentration (approx-

Fig. 8 Distributions of inclusions enriched by a specific compound. (*: Number of the inclusions in the region with manganese concentration lower than a specific value divided by the their total number in a spot-like segregation).

imately the same as C_L^{90} for Mn shown at the bottom line in Table 1) was defined as a spot-like segregation. They found that the maximum Mn concentration increases drastically when the diameter of a spot-like segregation exceeds $270\text{ }\mu\text{m}$ (Fig. 9) and that this is due to the occurrence of MnS precipitation⁽²⁵⁾. To compare the present model with this finding, the calculation was conducted for additional cases other than $L=100$ and $1000\text{ }\mu\text{m}$. The calculated results showed that MnS precipitation begins at the fraction liquid of approximately 1% when L exceeds $300\text{ }\mu\text{m}$ (Fig. 10). If MnS can be assumed to be spherical, its diameter can be estimated from the calculated amount of MnS. They are 5, 9 and $13\text{ }\mu\text{m}$ for $L=200$, 300 and $400\text{ }\mu\text{m}$, respectively. Since the observation by Fukuda *et al.* was conducted by a two-dimensional microanalyzer⁽²⁷⁾ based on EPMA with the electron beam diameter of $10\text{ }\mu\text{m}$, MnS with the diameter of $5\text{ }\mu\text{m}$ may not have been detected in many cases. From this consideration, it can be concluded that the calculated results (Fig. 10) are in good agreement with the observation (Fig. 9).

2. Model utilizing CALPHAD method

The above-mentioned coupled precipitation model is a universal model in principle in which any solute and compound precipitation can be considered. However, regarding the calculation of the equilibrium, more general methods have already been developed in the field of computer simulation of phase diagrams, CALPHAD (CALculation of PHase Diagram)⁽²⁸⁾⁽²⁹⁾. In this field, thermodynamic data^{(30)–(33)} and the integrated system⁽³⁴⁾ have been being consolidated. Their utilization in the process simulation is to be expanded⁽³⁵⁾⁽³⁶⁾. The present author

Fig. 9 Maximum manganese concentration in a spot-like segregation as a function of its diameter (observed relation)⁽²⁵⁾.

Fig. 10 The temperature and fraction liquid at the start of MnS precipitation and the temperature at $f_s=0.999$ (calculated values)⁽¹⁹⁾.

and coworkers also are developing models which utilize them.

The first model developed for the solidification of plain carbon steels is as follows⁽³⁷⁾. Equation (4) is used to calculate the increment of dissolved solute in the liquid due to the increase of solid by df_s , and C_L^i 's are renewed. Regarding the inclusions, a part of the inclusions calculated at the previous step are assumed to go into the solid in proportion to df_s . By the summation of the renewed dissolved solute and the inclusions left in the liquid, the total amount of solutes in the residual liquid is obtained. To these solute composition SOLGASMIX⁽²⁹⁾ (the name of computer program for thermodynamic equilibrium calculation) is applied, and the amounts of compounds in inclusions and dissolved solutes are calculated in equilibrium at the present step, where the consistency is satisfied between the temperature used in equilibrium calculation and the liquidus temperature calculated by the use of Hirai's equation⁽³⁸⁾ for the C_L^i 's which is obtained after the equilibrium calculation. In addition, from the predetermined cooling rate and the temperature difference between the previous and present steps, the time elapsed dt for the increment df_s can be calculated, and the dt/df_s value is used as t_s in the α and Ω calculations in the next step. This model is also applied to the sulfide shape control in anti-HIC steel by the Ca addition and the results obtained (Fig. 11) are similar to those by the coupled precipitation model.

In the next, the author *et al.* developed a more generalized model in collaboration with Sundman, who developed Thermo-Calc (computer software for phase

Fig. 11 Changes of the amounts of dissolved solutes (a) and non-metallic inclusions (b) during solidification of a spot-like segregation, calculated by the use of SOLGASMIX with consideration of valid range of $e_j^{(i)(37)}$.

diagram simulation)⁽³⁹⁾, which can be applied to solidification of high alloys including stainless steels⁽⁴⁰⁾. Method was developed to realize eq. (4) in a discrete manner by the use of Thermo-Calc. As the first step, Scheil's equation, eq. (2), can be realized in a discrete manner as follows: Firstly, a small amount of solid phase is precipitated by reducing the temperature a little bit below the liquidus temperature. Secondly, the precipitated solid is discarded out of the system and the temperature of the residual liquid is reduced a little bit again in order to precipitate a small amount of new solid phase. Then, the precipitated solid is discarded out of the system again. By repetition of these procedures, eq. (2) is realized. In the next step, we would like to introduce the effect of back diffusion into solid, i.e., to realize eq. (4). When eq. (4) is compared with eq. (2), the left hand side is the same, which corresponds the amount of rejected solute due to the progress of solidification. Only by the term $2\Omega k_f dC_L$, the right hand side is different from that of eq. (2), which

corresponds to the amount of solute consumed by back diffusion. Therefore, by equating the right hand sides of both equations, the relation is derived between the increments of dissolved solutes predicted by eqs. (4) and (2), $\Delta C_{L,C-K}$ and $\Delta C_{L,Sc}$:

$$\Delta C_{L,C-K} = (1 - f_s) / \{1 - (1 - 2\Omega k) f_s\} \Delta C_{L,Sc} \quad (13)$$

where $\Delta C_{L,Sc}$ is obtained by the difference of C_L at the present and previous steps in the discrete procedure mentioned above for eq. (2). Practically speaking, firstly the amount of increment of matrix solid and nonmetallic inclusions and dissolved solute contents are calculated in the equilibrium calculation at a set temperature, and the increment of C_L^i from the previous step gives the $\Delta C_{L,Sc}$. Secondly the $\Delta C_{L,Sc}$ is modified to $\Delta C_{L,C-K}$ by the use of eq. (13) in consideration of the back diffusion effect, and C_L in the present step is corrected by the use of the modified increment, $\Delta C_{L,C-K}$. Nonmetallic inclusions are assumed to distribute homogeneously throughout the residual liquid and the newly precipitated matrix solid, and the total solute content of each element in the residual liquid is calculated for the next step analysis from the modified content of dissolved solute and the amount of inclusions left in the liquid. In the next step analysis, the matrix solid and the inclusions in it are discarded out of the system and then the equilibrium calculation is carried out at a different temperature. By combining the increment Δf_s and the reduction ΔT from the previous step, and the predetermined cooling rate R , the instantaneous t_s value is calculated as $t_s = \Delta T / (R \cdot \Delta f_s)$ and reflected in α and Ω calculation, which is the same as the previous model. By these procedures, eq. (10) in the case with inclusions and eq. (4) in the case without inclusions can be integrated.

The method was applied to the solidification of 21%Cr–11%Ni stainless steel with 0.1%Si, 0.002%Al, 0.002%Ca and 0.005%O (mass percent) and solute segregation and chemical compositions change of inclusions were analyzed. The results are shown in Figs. 12 through 14. They are for $L = 100 \mu\text{m}$, $t_s = 100 \text{ s}$. Sub-lattice model is used as thermodynamic models for the liquid, δ and γ phases. Energy parameters for minor elements, Al, Si, O and Ca, are converted by the method proposed by Hillert⁽⁴¹⁾ from interaction parameters in the dilute solution model. The values for standard formation energy of stoichiometric compound were based on the SGTE database⁽³²⁾ and the cell model⁽⁴²⁾ was applied to multicomponent oxide liquid solution. In Fig. 12, δ phase precipitates as a primary phase initially and both δ and γ phases precipitate after it reaches the eutectic trough. The variation rates of dissolved solute contents change discontinuously when it reaches the eutectic trough. Especially, Cr content decreases when only the δ phase solidifies, but increases later at the eutectic solidification. The detailed behavior of dissolved solute contents and nonmetallic inclusions can be analyzed as shown in Figs. 13 and 14.

Fig. 12 Changes of the amounts of dissolved Cr and Ni in the liquid during solidification of a stainless steel analyzed by a Model combined with Thermo-calc⁽⁴⁰⁾.

Fig. 14 Changes of the amounts of nonmetallic inclusions in the same residual liquid as in Fig. 12⁽⁴⁰⁾.

Fig. 13 Changes of the amounts of dissolved O, Si and Al in the residual liquid during solidification of the same stainless steel as in Fig. 12⁽⁴⁰⁾.

IV. Combined Method of FDM for Solute Diffusion and Equilibrium Simulation in Each Segment

As availability of computation increases from the viewpoints of both capability of hardware and economics, a combined method becomes practical progressively, where the process to be analyzed is divided into segments and the transport phenomena between the segments and the reactions in each segment are solved interactively. As an first step, Koseki *et al.* analyzed the solidification path of the weld pool of stainless steels, where the transverse section of a growing dendrite is divided into finite elements as shown in Fig. 15 and the solute diffusion was analyzed by FDM and equilibrium calculation was car-

ried out in each element at each time step⁽⁴³⁾. By this method they could calculate the S/L interface movement and the solute distribution properly during solidification. However, they found that equilibrium could not be assumed for each element they used regarding the δ - γ transformation below approximately 1473 K. Therefore, they applied the Clyne-Kurz type formalism again in each element to the δ - γ transformation. That is, within the δ phase in a element the complete mixing of solutes was assumed and the limited back diffusion into the γ phase was manipulated by the use of the formalism. Between the adjacent elements, solute diffusion was solved by the FDM only in the δ phase and solute diffusion in the γ phase between the adjacent elements is neglected. Since the diffusion in the δ phase is active, the complete mixing in such a short distance as within a element and limited diffusion in such a long distance as over many elements are reasonable to be assumed for the δ phase, and since the diffusion in the γ phase is not so active as in the δ phase, the limited diffusion in each element and neglect of inter element diffusion is also reasonable to be assumed for the γ phase. An example of the calculated Ni and Cr distributions over the transverse section of a dendrite is shown in Fig. 16, in good agreement with those measured by Brooks *et al.*⁽⁴⁴⁾ with STEM. Figure 17 shows a comparison between the calculated and observed amounts of the residual δ phase, both being in fairly good agreement.

V. Conclusions and Remarks for Future Tasks

This paper is intended to present the current researches on its subject matter, in giving special emphasis to the work of the present author and coworkers. From this viewpoint, the author wishes to ask your patience in not referring to some important research work to be mentioned.

Among the items to be considered, in the future are the

Fig. 15 Model for transverse cross-section of dendrite (a) and schematic diagram for calculation method (b)⁽⁴³⁾.

morphology evolution in solidification, kinetics of nucleation and growth of nonmetallic inclusions, inclusion push-out at the interface, and diffusion and reactions within inclusions. Further, since the origin of nonmetallic inclusions goes up to deoxidation proc-

Fig. 16 Comparison between calculated and measured distributions of Cr and Ni in transverse cross-section of a dendrite⁽⁴³⁾. STM measurement was done by Brooks *et al.*⁽⁴⁴⁾

Fig. 17 Comparison between calculated and observed fractions of residual δ phase⁽⁴³⁾.

essing, analyses must be done until the initiation of solidification by following every process as well as after the solidification processing. Therefore the items to be solved are huge. However, it is considered important to make the effort to sort out tractable phenomena one by one to tackle the whole. For example, regarding the solidification, it is considered to be practical and improve precision to step up the model mentioned in Chapter IV, where precipitation reaction models (nucleation and growth) are treated in each element while the conduction of heat and the diffusion of solutes are solved between

elements by the FDM, and the time evolution of solute distribution and precipitation can be clarified. If inclusion push-out by the S/L interface can be modeled with considerations of interface energies of an inclusion for liquid and solid matrix, size, mass and shape of the inclusion, the velocity of the interface, etc., the amount of inclusions left at the residual liquid can be calculated more precisely. The diffusion and reactions in the inclusions can be analyzed by the use of the FDM in parallel with the analysis of solidification. Further, deoxidation process can also be analyzed in a similar way by dividing the reaction vessel into some segments, where the transport phenomena including liquid flow must be considered between the segments, precipitation, coagulation and flotation of inclusions must be modeled in each segment and reactions between slag and metal, refractory and metal, etc. must be modeled as interfacial reaction between segments, as an example. The author is also going to improve and develop methods for better analysis along this line.

REFERENCES

- (1) O. Haida, T. Emi, K. Sanbongi, T. Shiraishi and A. Fujiwara: *Tetsu-to-Hagané*, **64** (1978), 1538.
- (2) H. Nakasugi, S. Sugimura, H. Matsuda and T. Murata: *Seitetsu Kenkyu*, (1979), No. 297, 72.
- (3) O. Haida, T. Emi, G. Kawanishi, M. Naito and S. Moriwaki: *Tetsu-to-Hagané*, **66** (1980), 354.
- (4) T. Shiraiwa, N. Fujino and F. Matsuno: *The Sumitomo Serch.*, (1974), No. 11, 85.
- (5) N. Okushima: 126th and 127th Nishiyama Memorial Lecture, *Iron Steel Inst. Jpn.*, (1988), p. 145.
- (6) J. Takamura and S. Mizoguchi: *Proc. 6th Int. Iron and Steel Cong.*, **1** (1990), p. 591.
- (7) S. Mizoguchi and J. Takamura: *Proc. 6th Int. Iron and Steel Cong.*, **1** (1990), p. 598.
- (8) E. Scheil: *Z. Metallk.*, **34** (1942), 70.
- (9) H. D. Brody and M. C. Flemings: *Trans. Metall. Soc. AIME*, **236** (1966), 615.
- (10) T. W. Clyne and W. Kurz: *Metall. Trans. A*, **12A** (1981), 965.
- (11) T. Matsumiya, H. Kajioka, S. Mizoguchi, Y. Ueshima and H. Esaka: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 873.
- (12) Y. Ueshima, S. Mizoguchi, T. Matsumiya and H. Kajioka: *Metall. Trans. B*, **17B** (1986), 845.
- (13) Y. Ueshima, N. Komatsu, S. Mizoguchi and Y. Kajioka: *Tetsu-to-Hagané*, **73** (1987), 1551.
- (14) S. Kobayashi, T. Nagamichi and K. Gunji: *Trans. Iron Steel Inst. Jpn.*, **28** (1988), 543.
- (15) T. P. Battle and R. D. Pehlke: *Steelmaking Proc.*, **70** (1987), 121.
- (16) X. G. Wang, C. Dumortier and Y. Riquier: *Proc. 6th Int. Iron Steel Cong.*, **1** (1990), p. 705.
- (17) F. Matsuda, H. Nakagawa and J. B. Lee: *Trans. of JWRI*, **18** (1989), 1, 36.
- (18) I. Ohnaka: *Trans. Iron Steel Inst. Jpn.*, **26** (1986), 1045.
- (19) T. Matsumiya and T. Ohashi: *Tetsu-to-Hagané*, **71** (1985), S1069.
- (20) P. Nilles: *J. Iron Steel Inst.*, (1964), 601.
- (21) S. Stachura: *Archiwum Hutnictwa*, **29** (1984), 51.
- (22) J. Miettinen: *Scand. J. Metall.*, **17** (1988), 218.
- (23) S. Kitamura, H. Miyamura and I. Fukuoka: *Tetsu-to-Hagané*, **73** (1987), 677.
- (24) E. Ichise: *Tetsu-to-Hagané*, **77** (1991), 197.
- (25) Y. Fukuda, S. Mizoguchi, H. Kajioka and K. Arihara: *Tetsu-to-Hagané*, **71** (1985), S218.
- (26) L. E. K. Holappa and H. Ylönen: *Scanject III*, part 2 (1983), 47:1.
- (27) I. Taguchi, H. Hamada and S. Tani: *Seitetsu Kenkyu*, (1984), No. 313, 93.
- (28) M. Hasebe and T. Nishizawa: *Bulletin Japan. Inst. Metals*, **11** (1972), 879.
- (29) G. Eriksson: *Chemica Scripta*, **8** (1975), 100.
- (30) T. Nishizawa and M. Hasebe: *Tetsu-to-Hagané*, **67** (1981), 1887.
- (31) T. Nishizawa and M. Hasebe: *Tetsu-to-Hagané*, **67** (1981), 2086.
- (32) R. G. Gallanger, K. Hack, M. Simons and P. J. Spencer: *Steel Research*, **56** (1985), 7.
- (33) *Ironmaking and Steelmaking*, **11** (1984), 67.
- (34) C. W. Bale and G. Eriksson: *Can. Metall. Quat.*, **29** (1990), 105.
- (35) G. Eriksson and K. Hack: "SAGE", private communication.
- (36) B. Sundman: "CAMPADA", private communication.
- (37) W. Yamada, T. Matsumiya and A. Ito: *Proc. 6th Int. Iron Steel Cong.*, **1** (1990), p. 618.
- (38) M. Hirai, K. Kanemaru and H. Mori: The 19th committee on solidification, *Japn. Soc. Promotion of Sci., Solidification-46* (1968).
- (39) B. Sundman, B. Jansson, J-O. Andersson: *CALPHAD*, **9** (1985), 153.
- (40) W. Yamada, T. Matsumiya and B. Sundman: *Computer Aided Innovation of New Materials*, The First International Conference and Exhibition on Computer Applications to Materials Science and Engineering, Ed. by M. Doyama, T. Suzuki, J. Kihara and R. Yamamoto, North-Holland, Amsterdam, (1991), p. 587.
- (41) M. Hillert: *Metall. Trans. A*, **17A** (1986), 1878.
- (42) H. Gaye and J. Welfringer: *Second Int. Symp. on Metall. Slags and Fluxes*, Ed. by H-A. Fine and D. R. Gaskell, The Metal. Soc.-AIME, New York, (1984), p. 357.
- (43) T. Koseki, T. Matsumiya, W. Yamada and T. Ogawa: to be published.
- (44) J. A. Brooks: *Metall. Trans. A*, **14A** (1983), 23.
- (45) J. Lehman, H. Gaye, W. Yamada and T. Matsumiya: *Proc. 6th Int. Iron Steel Cong.*, **1** (1990), p. 256.