Experimental determination of partition coefficients considering peritectic reactions and application to macro-segregation simulation in a large steel ingot

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Partition coefficients are key parameters to predict compositional segregation in steel ingots. The random sampling method has been widely used to determine partition coefficients. However, no reports have been found that address Fe-based alloys involving a peritectic reaction. In this study, a new experimental method to obtain partition coefficients accounting for changes in partition coefficients associated with the peritectic reaction was developed.

A low-alloy steel exhibiting the peritectic reaction was employed in this study. The specimen was unidirectionally solidified and quenched during solidification. Two regions on a vertical cross-section were sampled before and after the peritectic reaction. Random sampling was applied to determine solute concentration profiles, and partition coefficients for each element were calculated through mass-balance analysis. The partition coefficients of Mn and Cr showed no significant change across the peritectic reaction. In contrast, those of Mo and V decreased, while that of Ni increased after the reaction. Solidification simulations of compositional segregation using the determined partition coefficients showed good agreement with the segregation in an actual large steel ingot.

KEYWORDS: PARTITION COEFFICIENT – PERITECTIC REACTION – RANDOM SAMPLING – MASS BALANCE ANALYSIS – UNIDIRECTIONAL SOLIDIFICATION – LOW ALLOY STEEL

INTRODUCTION: MEASUREMENT OF PARTITION COEFFICIENTS

Partition coefficients are key parameters for calculation of micro-segregation and macro-segregation (1-3). There are several methods to obtain partition coefficients, such as the CALPHAD approach (4,5) calculating equilibrium phase diagrams and thermodynamic quantities, or experimental methods analyzing solute distribution between solid and liquid phases. Experimental approaches include the equilibrium–quenching method (6,7), in-situ measurements using X-rays (8,9), and methods based on random sampling.

The random sampling method (10, 11) has been widely applied to determining partition coefficients. For Fe-based alloys, Yamamoto et al. (12) and Kobayashi et al. (13) measured partition coefficient in Fe-20Cr-25Ni-5Mo-1.5Cu alloys by combining random sampling with the Scheil-Gulliver's equation, Sumi et al.(14) investigated Fe-1C-8Cr-1.8Mo alloys, and Fukaya et al.(15) studied Fe-36Ni alloys. However, these studies focused on alloys exhibiting single-phase solidification. In contrast, low-alloy steels commonly used for large-scale products exhibit a peritectic reaction, which changes solute distribution between solid and liquid from δ/L to γ/L during solidification, resulting in the dramatic changes in the partition coefficients. Consequently, fitting based on the Scheil-Gulliver's equation assuming a constant partition coefficient is not applicable. On the other hand, Mass Balance Analysis (MBA) has been proposed as a method capable of accounting for variations in partition coefficients during solidification. Nevertheless, reported applications (16) have been limited to alloy systems that undergo single-phase solidification, such as Co-10Cu and Fe-0.57C-25Cr-35Ni-1Mn-1.25Si-0.5Nb alloys.

As described above, no reports have been found that address Fe-based alloys involving the peritectic reaction, and many aspects remain unclear regarding the applicability of the random sampling method to these alloys. Therefore, in the present study, an experimental method accounting for changes in partition coefficients associated with the peritectic reaction was developed by combining a random sampling method, mass-balance

analysis, and unidirectional solidification.

EXPERIMENTS AND RESULTS

A. Unidirectional Solidification experiments

The chemical composition of the sample used in this study is shown in Table 1. Thermo-Calc. calculations using the TCFE14 database estimated the liquidus temperature (T_L) to be 1502°C, the peritectic reaction temperature (T_P) to be 1474°C and the solid fraction at T_P ($f_{S\text{-}P}$) to be 0.59.

Tab. 1 - Chemical composition of low-alloy steel sample (mass%).

Chemical composition (mass%)						
C	Si	Mn	Ni	Cr	Mo	V
0.28	0.11	0.86	0.55	1.22	1.35	0.25

An electric resistance furnace equipped with a vertically movable specimen stage and a water bath for cooling at the bottom was used in this study (Figure 1). Withdrawing the stage enables unidirectional solidification of the sample from the bottom to the top. Approximately 150 grams of a low-alloy steel sample contained in an alumina crucible (outer diameter: 15 mm, inner diameter: 13 mm, and height: 250 mm) was heated and melted at 1600°C in an Ar atmosphere. This experiment consisted of two steps: a temperature measurement step and a quenching step. In the temperature measurement step, an R-type thermocouple with an alumina sheath was used to measure the sample temperature during unidirectional solidification (at a stage withdrawal rate of 1.67 mm/min). Measured positions were fixed at 85 mm and 125 mm from the sample bottom. Then the specimen stage was moved to the start position, the sample was re-melted, and the thermocouple was removed. In the quenching step, the specimen stage was withdrawn at 1.67 mm/min, and the sample was unidirectionally solidified again. When the temperature at 125 mm from the bottom reached the liquidus temperature (1502°C), the specimen was dropped into the water bath and quenched.

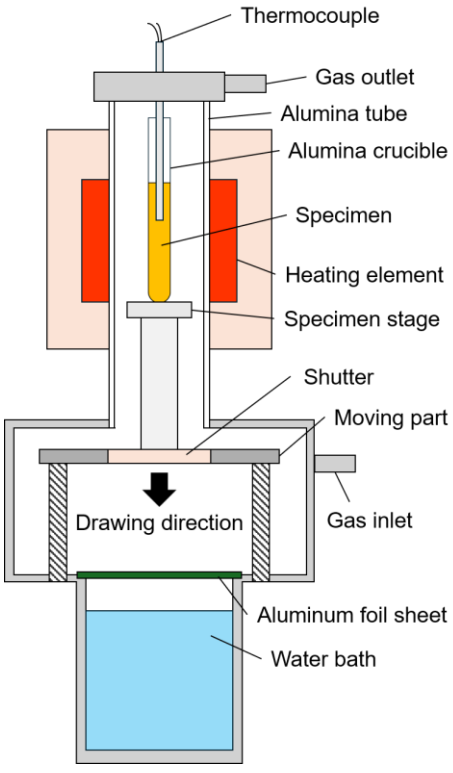

Fig. 1 - Schematic view of the vertical electric resistance heating furnace.

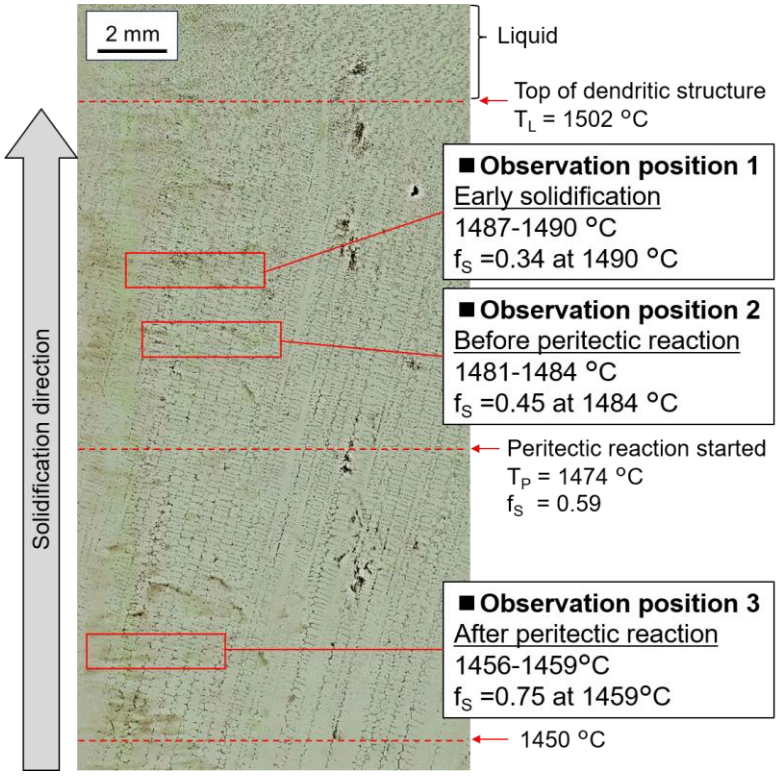

Fig. 2 - Temperature distribution on the vertical cross section of the sample and observation positions for EPMA.

B. Microstructure and EPMA observations

The quenched specimen above the height of 85 mm from the bottom was cut longitudinally through the center of the specimen. One half was etched for observation of the dendritic microstructure. The other half was used with an electron probe microanalyzer (EPMA). The dendritic microstructure and EPMA positions are shown in Figure 2. In this figure, the temperature distribution was estimated from the temperature measurement step by assuming that the temperature of the dendrite tip was equal to the liquidus temperature. Solid fractions in each observation position were calculated using Thermo-Calc.

EPMA measurements were conducted on an area of 1 mm in height and 4 mm in width. Figure 3 shows the EPMA mappings of Mo, V and Ni at position 3. Regions with high Mo and V concentrations were observed at the center of the dendrite arms. In contrast, the Ni concentration at the same locations was lower. This behavior indicates the solute redistribution associated with δ-to-γ transformation during the peritectic reaction.

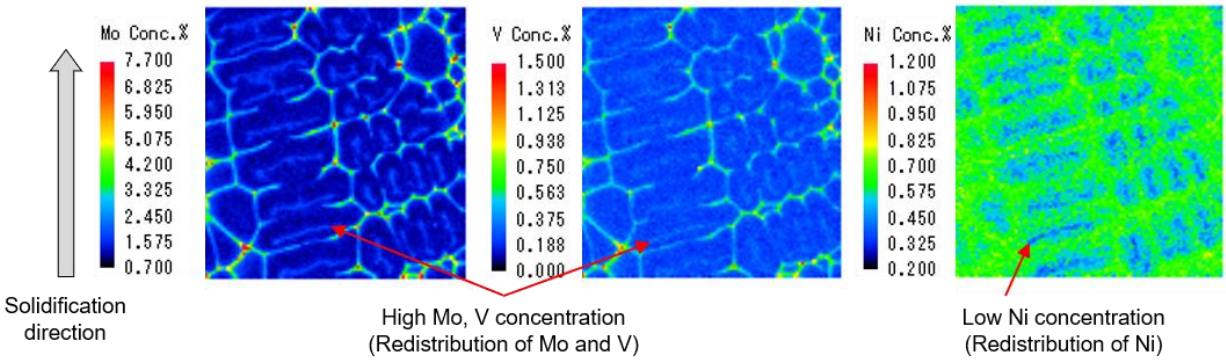

Fig. 3 - Solute redistribution observed at position 3 using EPMA.

C. Equilibrium-quenching experiments

The equilibrium partition coefficients were measured using the equilibrium-quenching method (referred to as the conventional method). Table 2 shows the chemical compositions of the specimens and their TL and TP calculated using Thermo-Calc. The chemical compositions of sample Eq-δ were similar to the compositions listed in Table 1, which showed δ-phase solidification, and those of sample Eq-γ simulated the composition in the liquid phase after peritectic reaction, which indicated primary γ-phase solidification. The specimen was held just below T_L to form a solid-liquid coexistence state and then maintained under this condition for 90 min to bring the solid-liquid interface close to equilibrium. After that, the specimen was water-quenched, and solute distributions on the cross-section of the specimen were measured using EPMA. Partition coefficients were determined from the ratio of the average solute concentrations in the solid and liquid phases.

Tab. 2 - Chemical composition of measurement samples for the conventional method.

Chemical composition (mass%) and liquidus, peritectic reaction temperature (°C)									
	C	Si	Mn	Ni	Cr	Mo	V	T_L	T_P
Sample Eq-δ	0.27	0.05	0.81	0.53	1.19	1.36	0.27	1504	1475
Sample Eq-γ	1.02	0.15	1.46	1.01	2.33	3.66	0.65	1429	-

DISCUSSION

A. Random Sampling method

Since sorting errors of random sampling are strongly influenced by the sorting methods, the appropriate sorting method for the present measurement was investigated. In the following analyses, concentration maps were smoothed using a 3 x 3 point average to reduce scatter. Due to significant solute redistribution as shown in Figure 3, Mo, V and Ni were unsuitable as sorting elements. Therefore, Fe, Mn and Cr sorting were examined. Figure 4 shows concentration profiles up to the solid-liquid interface for position 2 (before peritectic reaction)

and position 3 (after peritectic reaction) sorted by Fe, Mn and Cr. The vertical axis represents the ratio of the measured concentration, C_S, to the average concentration of the observation area, $C_{Ave.}$ For simplicity, profiles were averaged at solid fraction intervals of 0.01.

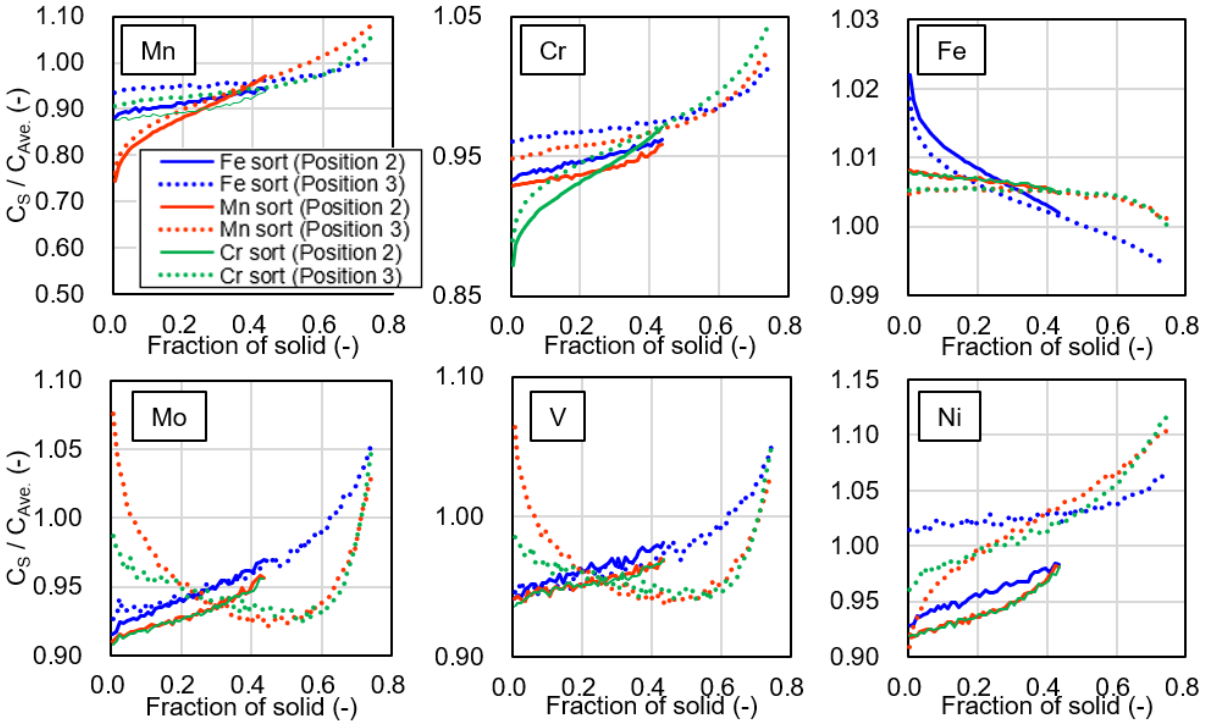

Fig. 4 - Comparison of concentration profiles among sorting elements.

Sorting a concentration profile by the same element generates an extreme concentration gradient termed as "slope segment" at low solid fractions due to EPMA scatter (11).Therefore, Cr or Fe sorting is appropriate for the Mn profile, while the Cr profile is better evaluated using Mn or Fe sorting. Profiles of Mo, V and Ni sorted by Mn were consistent with those using Cr sorting, while profiles obtained by Fe sorting were shifted toward a higher concentration compared with those sorted by Mn or Cr. Thermo-Calc. calculation estimates that the partition coefficient of Fe is only 1.01-1.02, resulting in very small concentration changes in the solid phase. Consequently, sorting errors of Fe were larger than those of Mn and Cr.

The profiles at position 3 of Ni, V and Mo exhibited different tendencies depending on the sorting elements. Profiles using Fe sorting showed a monotonically increase with the solid fraction. In contrast, profiles sorted by Mn or Cr indicated high concentrations of Mo and V near the solid fraction of zero, while for Ni profiles using Mn and Cr sorting, particularly low concentrations were observed near $f_S = 0$. The concentrations in the solute redistribution regions (Figure 3) and those near $f_S = 0$ in the concentration profiles (Figure 4) are compared in Table 3. Mn sorting showed the closest agreement with the measured values. Therefore, it is considered that Mn is the most appropriate element for sorting the present results.

Tab. 3 - Comparison of concentration ratios among sorting elements in the solute redistribution regions.

Comparison of concentration ratios			
	Mo	V	Ni
Measurement	1.07	1.04	0.80
Fe sort	0.93	0.95	1.01
Mn sort	1.05	1.04	0.92
Cr sort	0.98	0.98	0.96

B. Mass Balance Analysis

The MBA method determines concentration in the liquid phase by calculating the solute mass in the liquid phase from the total solute mass in the system minus the solute mass in the solid phase. Equations for MBA are shown below.

$$C_{L(f_S)} = \left\{C_0 - \int_0^{f_S} C_{S(f_S)} df_S\right\} / (1 - f_s) \quad [1]$$

$$k_{(f_S)} = C_{S(f_S)} / C_{L(f_S)} \quad [2]$$

Here, $k(f_S)$ is the partition coefficient at f_S, $C_S(f_S)$ is the solute concentration on the solid side of the solid-liquid interface at f_S, which can be obtained by random sampling, $C_L(f_S)$ is the solute concentration in the liquid phase at f_S, and C_0 is the initial concentration in the system. To minimize the effect of solute migration after solidification on the calculation, the partition coefficients were determined near the solid-liquid interface in each position.

The determined partition coefficients in this study are compared with those obtained from the conventional method in Figure 5. The sorting method combining Mn and Cr, which used Cr only for the sorting Mn profiles (referred to as Mn-Cr sorting) and Fe sorting were used. The results using Mn-Cr sorting were compared with the equilibrium partition coefficients. The results by Fe sorting were compared with the Mn-Cr sorting results to evaluate the influence of sorting errors.

Since the partition coefficients for the δ-phase solidification using the conventional method were measured just below T_L, it is considered that they are close to the partition coefficients at the initial state of solidification. However, the values measured by the present method at position 1 tended to be larger than the equilibrium values and close to unity. Previous studies reported that partition coefficients measured using random sampling tended to approach unity compared with equilibrium values (12-14). Micro-segregation is reduced by back diffusion in many cases, resulting in deviations from the Scheil-Gulliver's model. Consequently, when the Scheil-Gulliver's equation is used to obtain partition coefficients, the calculation result is fitted to the reduced micro-segregation, causing the calculated partition coefficients to approach unity. For example, partition coefficients measured using random sampling showed a dependence on the cooling rate (12, 14).

On the other hand, regarding changes in the partition coefficients from δ-phase to γ-phase solidification, the trends obtained using the present method were consistent with those of the equilibrium values. For example, the partition coefficients for Cr, Mo and V during γ-phase solidification were lower than those during δ-phase solidification, whereas those for Mn and Ni during γ-phase solidification were higher than those during δ-phase solidification.

Some differences in partition coefficients between Fe sorting and Mn-Cr sorting were observed due to sorting errors associated with Fe sorting. Nevertheless, the maximum difference between the two methods was only 0.03 even after the peritectic reaction, suggesting that rough estimation of partition coefficients may be possible near the solid-liquid interface even if the Fe sorting profiles cannot simulate solute redistribution. This is because the Fe concentration near the solid-liquid interface at position 3 was enough low to distinguish measurement points near the solid-liquid interface from the other points, as shown in the Fe profile sorted by Mn shown in Figure 4.

Based on the above results, it appears that the present measurement method can obtain the partition coefficients and simulate those changes from δ-phase to γ-phase solidification induced by the peritectic reaction. However, the partition coefficients measured by the present method tended to approach unity relative to the equilibrium partition coefficients due to back diffusion. Conversely, the values determined by the present method may also be regarded as fitting parameters for an actual micro-segregation calculation affected by a lot of solidification conditions. Therefore, by appropriately selecting solidification conditions, this method may be applicable as a direct evaluation technique for micro-segregation ranging from equilibrium solidification to the Scheil-Gulliver's model.

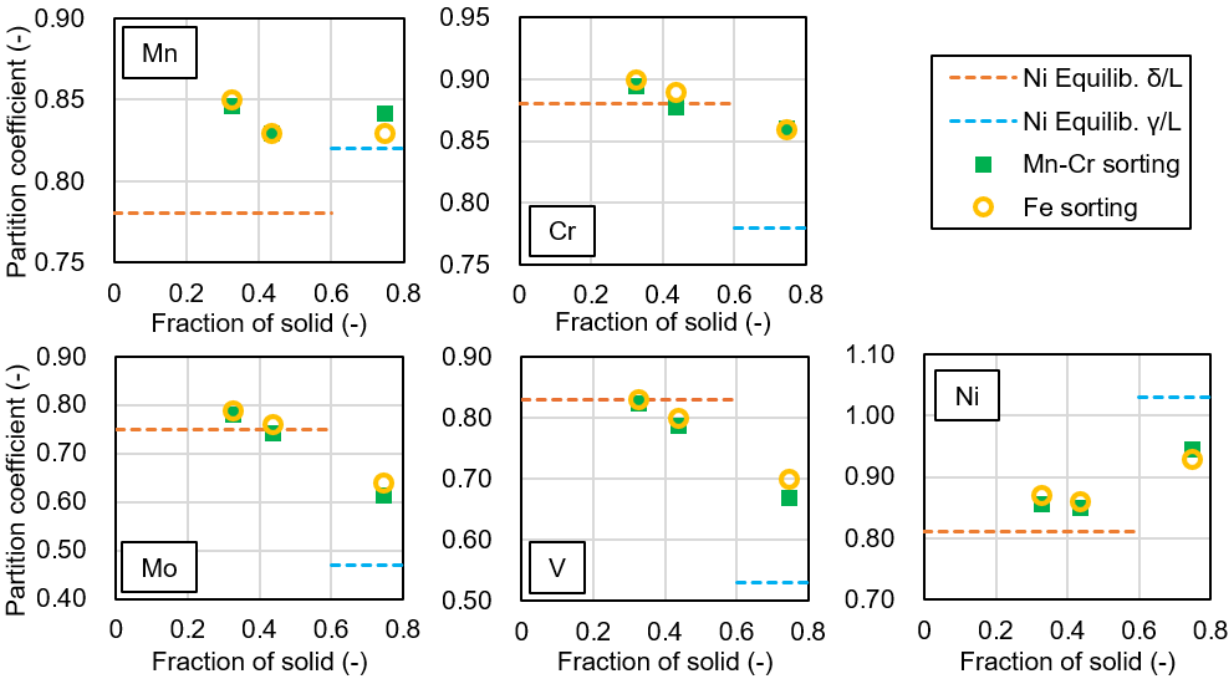

Fig. 5 - Comparison of partition coefficients among equilibrium values, MBA using Mn-Cr sorting and Fe sorting.

C. Calculation of Macro-segregation

To calculate micro-segregation for Fe-based alloys involving the peritectic reaction, not only partition coefficients of δ-phase and γ-phase but many additional parameters, including diffusion coefficients and the migration velocity of the δ-γ interface, are required (17). Consequently, incorporating the peritectic reaction into the macro-segregation simulation is highly complex. It is considered that the partition coefficients measured by the present method are parameters including the effects of solute distribution, solute diffusion and migration of the δ-γ interface. Therefore, applying these values to the macro-segregation simulation may provide a simplified approach to accounting for the peritectic reaction. Accordingly, the partition coefficients measured using the present method were used to calculate the compositional segregation in the actual steel ingot weighing approximately 90 tons, and the capability of simulating the concentration distribution was evaluated. Table 4 shows the chemical composition of the large steel ingot for the calculation and the sample used for measurement of the partition coefficients. Table 5 summarizes the measured partition coefficients. Mn sorting was employed for random sampling, while only the Mn profile was sorted by Fe because solute redistribution was observed in the Cr map of this sample.

The calculation of macro-segregation was performed using the casting simulation software MAGMASOFT and MAGMAsteel, which can calculate thermal and solutal convection. The partition coefficients of carbon were calculated by Thermo-Calc, while the values listed in Table 5 were applied. The diffusion coefficients in the solid phase for each element were set to 1E-20 to suppress solute diffusion except for carbon. The permeability coefficient was determined by fitting calculated the carbon concentration to the measured concentration. The radial concentration distribution at a height of 2170 mm from the bottom of the ingot was employed for the comparison.

Figure 6 shows the comparison between the measured concentration and the calculation results. Although the calculated values were generally higher than the measured values, the radial variation in concentration was simulated well. These results indicate that the partition coefficients measured by the present method can potentially be used to calculate macro-segregation without the need for additional micro-segregation parameters.

Tab. 4 - Chemical composition of initial values for calculation and measurement sample.

Compositions for macro-segregation simulation and measurement of partition coefficients (mass%)						
	C	Si	Mn	Ni	Cr	Mo
Calculation composition	0.46	0.71	0.69	0.29	3.46	0.47
Measurement sample	0.42	0.68	0.66	0.27	3.40	0.46

Tab. 5 - Partition coefficients measured using the method established in this study.

Measured partition coefficients							
T (°C)	f_S (-)		Si	Mn	Ni	Cr	Mo
1482	0.07	δ/L	0.89	0.86	0.85	0.90	0.76
1471	0.26		0.88	0.84	0.83	0.87	0.71
1465	0.45	γ/L	0.85	0.87	0.92	0.88	0.65

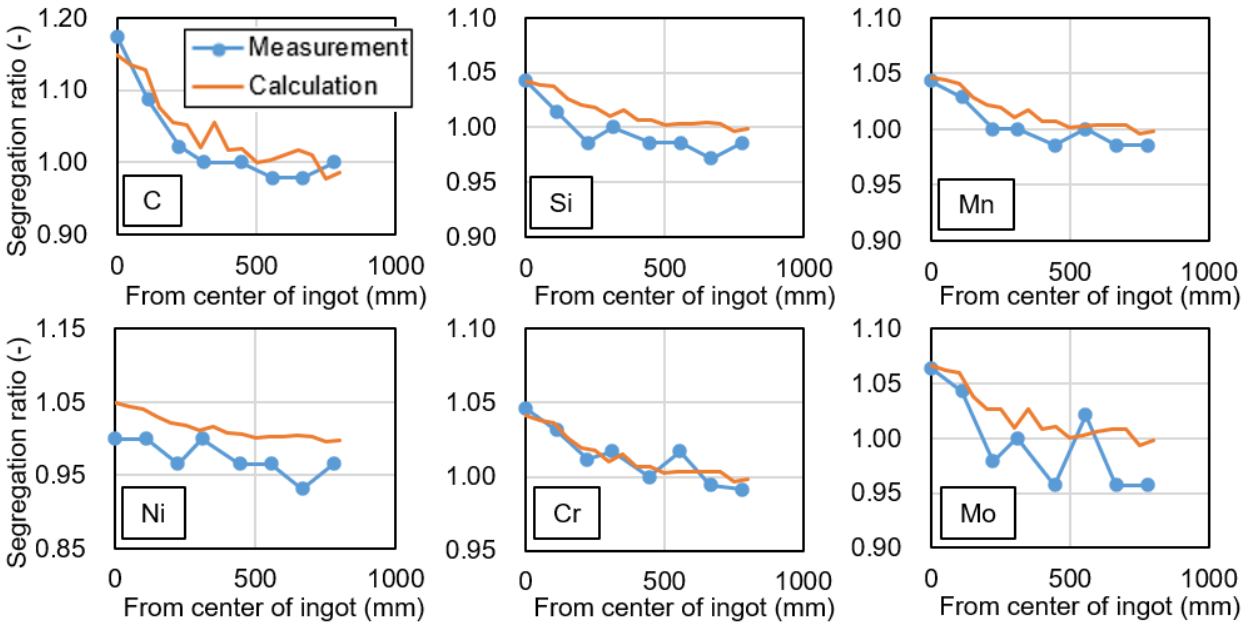

Fig. 6 - Comparisons between measurements of actual ingot and calculation results of macro-segregation.

CONCLUSION

1. Mn is the most appropriate element for random sampling in the present results. Fe-sorting profiles differed significantly from the measured distribution in the region of solute redistribution compared with profiles using Mn and Cr sorting.

2. The partition coefficients measured by the present method tended to approach unity relative to the equilibrium partition coefficients due to back diffusion. However, the tendency of change in partition coefficients from the δ-phase to the γ-phase measured by the present method was consistent with that of the equilibrium values.

3. The partition coefficients measured using the present method were applied to a macro-segregation simulation. The simulation was successful in closely calculating the trends of concentration changes

observed in the actual ingot, indicating the potential of the present method to calculate the micro-segregation and the macro-segregation involving the peritectic reaction without the need for complex parameters.

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