Quantification of manganese dendritic segregation in 380CL steel billet by electron probe microanalysis

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Abstract

Two methods are provided to accurately quantify the degree of manganese dendritic segregation in 380CL steel billet by using electron probe microanalysis, namely mapping analysis and line analysis. The quantitative accuracy of each pixel in mapping analysis is mainly investigated, and a series of experiments at different dwell times are carried out to optimize the parameter and reduce the error of quantitative analysis. Statistical analysis is used to calculate the characteristic segregation ratio value in the line or mapping analysis which can provide e.g. 12×10^4 values at about 4.3 mm^2 . The statistical number of data points in line analysis is studied in terms of length and position of analysis lines. For the specimens of 380CL steel billet, mapping analysis area of 1 mm^2 containing over 10 dendrites is recommended for quantifying the dendritic segregation of manganese. Six 2 mm lines along different directions containing about 2000 pixel points is also proposed for more accurate line analysis of Mn segregation.

Keywords Dendritic segregation · Quantitative method · Segregation ratio · Statistical analysis · EPMA

1 Introduction

During solidification of the liquid steel, dendritic growth virtually always causes some elements to concentrate in the inter-dendritic regions and leave the elements concentration lower in the dendritic regions, and the concentration difference will be called dendritic segregation. Banded microstructures arise in rolled plate due to dendritic segregation of some alloying element [1, 2], which has negative effects on mechanical and technological properties of the rolled steel products [2, 3]. In order to control the microsegregation, it's important to quantify the segregation accurately. Some studies [4–8] provided the quantitative distribution of alloying elements in the slab by electron probe microanalysis (EPMA). Statistical analysis [9] of EPMA results was used to find out characteristic values for segregated elements, however absolute values cannot be taken from EPMA readings because in all cases there will be a small number of concentrations below or above the chosen

extreme values. Non-metallic inclusions or precipitates like (MnS) will yield excess concentrations, which can be set as upper extreme value. Mn concentration can be below the detection limit (DL) corresponding to the applied dwell time (DL around 0.01 mass% for 60 s acquisition time), therefore, zero will generally be set as lower extreme value.

In the present study, quantitative analysis of Mn dendritic segregation in 380CL steel billet is carried out by EPMA, and statistical results of mapping and line analysis are compared and testified each other, aiming to get the most reliable experimental data of dendritic segregation. A key parameter as dwell time is mainly investigated especially for mapping analysis in order to obtain the accurate manganese concentration value for each pixel of the scanning area. The size and position of analyzed area are also examined to weaken the effect on the quantitative results of dendritic segregation. Whether the number of pixel points in the line analysis is adequate for representing the sample is further studied in the paper.

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2 Materials and methods

The transverse sample for experimental investigations was cut at the size of 18 mm (width) × 30 mm (length) × 20 mm (height) from 380CL billet, and then was grinded and polished metallographically. The chemical compositions of the investigated specimen are determined by optical emission spectrometry as follows in percentage by mass: 0.11 (± 0.01) %C, 0.010 (± 0.002) %Si, 0.94 (± 0.03) %Mn, 0.008 (± 0.001) %P, 0.0030 (± 0.0016) %S, and remaining Fe.

For the quantification of dendritic segregation, experiments were performed with a Shimadzu electron probe microanalyzer equipped with 4 wavelength dispersive spectrometers. Two analysis methods were utilized in this study, including mapping analysis method and line analysis method. The operating conditions applied throughout the present work were: accelerating voltage 20 kV, beam current 300 nA. The detailed experimental procedure is as follows:

1. Mapping analysis method

- Mapping analysis is firstly performed, characteristic X-ray intensity of Mn is recorded at each pixel of a pre-selected area and then the distribution of Mn element is plotted for the $x \times y (= N)$ pixels measured area of the steel billet.
- The calibration curve generated from a series of reference materials is used to quantify the Mn map by converting X-ray counts to concentrations.
- Import the data to Matlab or other software, and sort the pixels (1 – N) based on the calculated Mn concentrations from the lowest to the highest value and plot the cumulative distribution as pixel number i (1 to N) versus Mn concentration.
- Finally, calculate the segregation ratio (SR) of manganese according to Eq. (1).

$$SR = \frac{C_{high}}{C_{low}} \quad (1)$$

where

$$C_{high} = \frac{\sum_{N-K+1}^N C_i}{K}, \quad (2)$$

$$C_{low} = \frac{\sum_1^K C_i}{K}, \quad (3)$$

$$X = \frac{K}{N} \quad (4)$$

Among that, SR, ratio of high concentrations and low concentrations; C_{high} , mean concentration value between $(N - K + 1)$ to N ; C_{low} , mean concentration value between 1 and K ; K , pixel number between 1 and N (constant); X , threshold cumulative frequency, selected between 5 and 20% for the present study.

2. Line analysis method

- Line analysis are firstly performed respectively along several representative lines in a certain area of steel billet, and then the variation curve of Mn X-ray intensities is acquired along each line by stage movement pixel by pixel.
- The calibration curve generated from a series of reference materials is used to quantify the Mn line data by converting X-ray counts to concentration values.

The following procedure is identical to Step c and d in mapping analysis method.

For the two methods in the paper, Matlab-program is developed for the statistical analysis of dendritic segregation, and is designed to eliminate all excess concentrations from the mapping or lines belonging to non-metallic inclusions or precipitates like (MnS).

3 Results and analysis

3.1 Mapping analysis

3.1.1 Mapping analysis at different dwell times

- Error evaluation of quantitative analysis at different dwell times

A reference material of Fe–Mn alloy with 0.85%Mn was selected to evaluate the error of quantitative analysis at 15 different dwell times. The quantitative analysis was carried out by adopting standard calibrating curve method. For each dwell time, the statistical counts and Mn concentration were listed in Table 1. The corresponding relative standard deviation (RSD) of counts and relative error (RE) of Mn concentration were also calculated in the table compared to the reference value. As the dwell time delays from 10 ms to 10 s, the counts increase gradually from 41 to 41,645, relative standard deviation of counts decreases from 15.62 to 0.49, and Mn concentration intends to be stable at about 0.83%. At 0.5 s, the standard deviation of counts is 2.19% and relative error of Mn concentration is less than 3% which are acceptable for

Table 1 Quantitative results of reference material at 15 dwell times

Dwell time	Counts	RSD (%)	Mn (mass%)	RE (%)
10 ms	41	15.62	0.83	−2.4
20 ms	77	11.43	0.76	−10.6
30 ms	120	9.13	0.80	−5.9
40 ms	167	7.74	0.83	−2.4
50 ms	200	7.07	0.80	−5.9
70 ms	293	5.84	0.84	−1.2
100 ms	410	4.94	0.81	−4.7
150 ms	627	3.99	0.83	−2.4
200 ms	853	3.42	0.85	0
300 ms	1217	2.87	0.80	−5.9
500 ms	2078	2.19	0.83	−2.4
1 s	4194	1.54	0.84	−1.2
5 s	20,851	0.69	0.83	−2.4
10 s	41,645	0.49	0.83	−2.4

accurate quantification, so the dwell time of 0.5 s/point is selected for the following mapping analysis in 380CL billet in order to obtain a reliable result of Mn dendritic segregation although it may cost 17 h to complete the mapping analysis.

2. Mapping experiments

The mapping analysis was conducted at four dwell times as 30 ms/point, 50 ms/point, 100 ms/point, 500 ms/point based on counting statistics ($RSD < 10\%$), and the distribution maps of Mn segregation were acquired in Fig. 1 with horizontal 400 pixels and vertical 300 pixels. Obvious dendritic segregation of manganese can be observed at all dwell times from 30 ms/point to 500 ms/point, however the morphology of Mn segregation becomes more precisely with the extension of dwell time especially at 500 ms/point. The average counts increase from 138, 227, 483 to 2344 corresponding to 30 ms/point, 50 ms/point, 100 ms/point and 500 ms/point. The

Fig. 1 Mn maps at different dwell times: **a** 30 ms, **b** 50 ms, **c** 100 ms, **d** 500 ms

Fig. 2 Cumulative distribution of Mn concentrations at different dwell times

Fig. 3 Variation of segregation ratios with the extension of time

cumulative distribution of Mn concentrations at different dwell times are plotted in Fig. 2 as pixel number i (1 to N) versus Mn concentration. Generally, it indicates that the values of low concentrations zone increase and the values of high concentrations zone decrease gradually with the extension of dwell time. Obviously, Mn concentration value becomes more reliable due to more X-ray counts as the dwell time delays.

For different X values, the variation curves of segregation ratios with the extension of dwell time are plotted in Fig. 3. It is shown that SR decreases gradually with increasing threshold cumulative frequency X for all tested dwell times. SR tends to be stable from $X = 15\%$. Cumulative frequency $X = 15\%$ is assumed as the critical value of acquiring stable SR value, so it is adopted for the following analysis of 380CL billet in this study.

Furthermore, SR values trend to be decreasing and stable gradually as the dwell time delays for every X

values, for instance the variation of SRs is only 0.02% per unit millisecond after 100 ms at $X = 15\%$. Therefore, appropriate dwell time is considered to be important to obtain an accurate SR value of Mn element.

3.1.2 Mapping analysis at different measuring areas

The size of measuring area is 2.4 mm (X axis) $\times$ 1.8 mm (Y axis) containing 120 thousand data points for the investigated sample of 380CL billet in Sect. 3.1.1. When the measuring area reduces to 1.2 mm $\times$ 0.9 mm, it's 1/4 of the original area and includes 30 thousand data points; when the measuring area reduces to 0.6 mm $\times$ 0.45 mm, it's 1/16 of the original area and includes 7.5 thousand data points. Quantitative results for the sizes of 1.2 mm $\times$ 0.9 mm and 0.6 mm $\times$ 0.45 mm are calculated in Table 2.

Five 1.2 mm $\times$ 0.9 mm regions are analyzed separately, and the SR values are identical to the original one of 2.4 mm $\times$ 1.8 mm region with relative errors below 3%; eight 0.6 mm $\times$ 0.45 mm regions are analyzed with relative errors below 6% compared to the original SR value "1.23".

Taking into account of distribution maps of manganese at different areas (Fig. 4), two branches of coarse primary dendrites and five branches of secondary dendrites containing over 25 dendrites can be seen for the area of 2.4 mm $\times$ 1.8 mm, three branches of secondary dendrites containing over 10 dendrites exist in the area of 1.2 mm $\times$ 0.9 mm, whereas only one branch of secondary dendrites containing over three or four dendrites is in the area of 0.6 mm $\times$ 0.45 mm.

Therefore, it's advisable that analysis area isn't less than 1.2 mm $\times$ 0.9 mm and contains over 10 dendrites in order to ensure the accuracy and representativeness of quantitative analysis.

3.1.3 Mapping analysis at different measuring positions

The size of the investigated sample surface is 30 mm long and 18 mm wide, four positions were randomly selected at the space of 5–20 mm between them and Mn mapping analysis at four positions were completed (Fig. 5). Quantitative results of manganese segregation are shown in Table 3. That the SR values at four positions are almost identical implies that the degree of Mn segregation is close and uniform basically across the whole sample. So the quantitative analysis at a 1.2 mm $\times$ 0.9 mm area is virtually enough to characterize the dendritic segregation of manganese in the sample of 380CL billet.

Table 2 Quantitative results for different measuring areas

Measuring area	Region	C _{low} (mass%)	C _{high} (mass%)	SR	RE (%)
1.2 mm×0.9 mm	1	0.80	0.97	1.20	2.44
	2	0.83	1.02	1.23	0
	3	0.79	0.95	1.21	1.63
	4	0.81	1.00	1.23	0
	5	0.80	0.97	1.21	1.63
0.6 mm×0.45 mm	1	0.81	0.97	1.19	3.25
	2	0.81	0.99	1.22	0.81
	3	0.82	1.02	1.24	−0.81
	4	0.81	1.01	1.24	−0.81
	5	0.80	0.93	1.16	5.44
	6	0.82	1.00	1.22	0.98
	7	0.78	0.94	1.20	2.42
	8	0.82	0.98	1.21	2.03

Fig. 4 Mn maps at different areas: **a** 2.4 mm×1.8 mm, **b** 1.2 mm×0.9 mm, **c** 0.6 mm×0.45 mm

3.2 Line analysis

When quantifying the dendritic segregation by the method of line analysis, an adequate dwell time is practical

and easy to implement for the accuracy of quantitative analysis at each pixel point, since total measuring time isn't long due to a small quantity of data points which is far less than the number of mapping analysis in the whole

Fig. 5 Mn maps at four positions: **a** position 1, **b** position 2, **c** position 3, **d** position 4

Table 3 Quantitative results at different positions

Position	C_{low} (mass%)	C_{high} (mass%)	SR
1	0.80	0.97	1.20
2	0.88	1.07	1.22
3	0.83	1.03	1.24
4	0.82	0.99	1.21

area. In the following part, it's further studied whether the result of line analysis containing a limited number of data points could be representative for the measuring area in this paper.

3.2.1 Experiments of line analysis

In the same area as scanned by the mapping analysis, line analysis of Group A, B and C were carried out by choosing different setting of six lines, namely Group A includes 3 lines along X direction and 3 lines along Y direction separately equally divided the measuring area, Group

B includes 3 lines along X direction and 3 lines along Y direction randomly and Group C includes six oblique lines. Figure 6 shows the variation curves of Mn concentration along six lines of Group A, B and C one by one. All concentration values of six analysis lines of each group are exported to Matlab program for statistical analysis, and the cumulative distribution of Mn concentrations of Group A, B and C are plotted in Fig. 7 as pixel number i (1 to N) versus Mn concentration. The segregation ratios of mapping and line analysis are calculated in Table 4.

Quantitative data of mapping analysis is also listed in Table 4 as compared to the results of line analysis. The SR values of line analysis in Group A, B and C are identical to the SR value of mapping analysis considering the standard deviation.

3.2.2 Size of line analysis

As analyzed in Sect. 3.2.1, quantitative results of Group A, B or C are reliable to characterize the degree of Mn dendritic segregation in the investigated sample of 380CL billet.

Fig. 6 Variation curves of Mn concentration along six lines in Group A, B and C

Fig. 7 Cumulative distribution of Mn concentration of Group A, B and C

Table 4 Quantitative results of mapping and line analysis

Item	C_{low} (mass%)	C_{high} (mass%)	SR
Mapping analysis	0.80	0.99	1.23
Line analysis			
Group A	0.79	0.96	1.22
Group B	0.81	0.99	1.22
Group C	0.81	0.99	1.22

Table 5 Statistical results of line analysis at five areas of 1.2 mm × 0.9 mm

Area	C_{low} (mass%)	C_{high} (mass%)	SR	RE (%)
1	0.80	0.97	1.20	2.33
2	0.83	1.03	1.24	−0.73
3	0.78	0.95	1.22	0.82
4	0.81	0.98	1.22	0.99
5	0.81	0.95	1.17	4.75

The numbers of pixel points in Group A, B or C are 2091, 2106 and 1993 respectively. If the size of measuring area is reduced to 1/4 of the original size of 2.4 mm × 1.8 mm, namely that the length of each line along X direction is 1.2 mm and the length of each line along Y direction is 0.9 mm for Group A, the total number of pixel points is cut down to 1050. Then five different areas with the size of 1.2 mm × 0.9 mm were randomly selected, and six line analysis were performed for each area with statistical results acquired in Table 5. It indicates that the SR values of manganese at the five areas vary from 1.17 to 1.24 with relative error less than 5%.

Table 6 Statistical results of line analysis at eight areas of 0.6 mm × 0.45 mm

Area	C_{low} (mass%)	C_{high} (mass%)	SR	RE (%)
1	0.82	0.95	1.17	4.88
2	0.81	0.98	1.21	1.63
3	0.80	0.96	1.19	3.25
4	0.81	1.03	1.27	−3.25
5	0.81	0.91	1.13	8.29
6	0.81	0.99	1.22	1.16
7	0.78	0.92	1.18	3.70
8	0.82	0.97	1.18	3.85

Adopting the similar method as mentioned above, the size of measuring area is reduced to 1/16 of the original size of 2.4 mm × 1.8 mm, namely that the length of each line along X direction is 0.6 mm and the length of each line along Y direction is 0.45 mm for Group A, and the total number of pixel points is cut down to 525. Then eight different areas with the size of 0.6 mm × 0.45 mm were randomly selected, and six line analysis were performed for each area with statistical results acquired in Table 6. It indicates that the SR values of manganese at the eight areas vary from 1.13 to 1.27 with relative error ranged from 1 to 10%.

So considering the error of quantitative analysis, the size of 1.2 mm × 0.9 mm containing about 1000 pixel points is at least required for the quantitative line analysis of Mn dendritic segregation in the sample of 380CL billet. Given that total measuring time (e.g. 1.5 h) is acceptable with the size of 2.4 mm × 1.8 mm, six 2 mm lines along different directions containing about 2000 pixel points is here recommended for more accurate analysis of Mn segregation.

4 Conclusion

Accurate mapping analysis and representative line analysis are mainly studied in the specimen of 380CL steel billet in this paper.

1. In order to quantify Mn dendritic segregation accurately, it's necessary to consider adequate counts at each pixel point for an acceptable standard deviation in mapping analysis despite a long run time. 0.5 s/point dwell time was selected, and about 2000 counts at each pixel and 2% standard deviation of counts are found to be reliable for the quantification of Mn dendritic segregation in this study.
2. The degree of Mn segregation is mostly uniform across the whole sample, and it's advisable that analysis area

isn't less than 1 mm² containing over 10 dendrites for the quantitative characterization of manganese segregation.

3. Line analysis of Group A, B and C with different setting for analysis lines are testified to be reliable and representative for the investigated sample. Six 2 mm-long lines along different directions containing about 2000 pixel points is recommend for more accurate analysis of Mn dendritic segregation. Line analysis could be very feasible for practical use because of a short measuring time.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Verhoeven JD (2000) A review of microsegregation induced banding phenomena in steels. *J Mater Eng Perform* 9:286–296
2. Krauss G (2003) Solidification, segregation, and banding in carbon and alloy steels. *Metall Mater Trans B* 34B:781–792
3. Grange RA (1971) Effect of microstructural banding in steel. *Metall Trans* 2:417–426
4. Yamashita T, Torizuka S, Nagai K (2003) Effect of manganese segregation on fine-grained ferrite structure in low-carbon steel slabs. *ISIJ Int* 43(11):1833–1841
5. Matsumiya T, Kajioka H, Mizoguchi S, Ueshima Y, Esaka H (1984) Mathematical analysis of segregations in continuously cast slabs. *Trans ISIJ* 24:873–882
6. Preßlinger H, Mayr M, Tragl E, Bernhard C (2006) Assessment of the primary structure of slabs and the influence on hot- and cold-rolled strip structure. *Steel Res Int* 77(2):107–115
7. Rezende J, Siquieri R, Emmerich H et al (2009) Prediction of microstructure and microsegregation in a Fe–Mn–C austenitic steel based on phase-field microstructure simulations. *Steel Res Int* 80(9):609–615
8. Llie S, Preßlinger H, Reisinger P, Mayr M, Etzelsdorfer K (2007) Results of research into the segregation behaviour of manganese, silicon and chromium in continuous casting. *Steel Res Int* 78(4):327–332
9. Senk D, Erdem E, Stratemeier S (2009) Statistical analysis of EPMA results for numerical modelling of micro-segregation in steel. *Int J Cast Met Res* 22(1–4):94–98

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