Influence of Calcium-treatment on Sulfide- and Oxide-inclusions in Continuous-cast Slab of Clean Steel —Dendrite Structure and Inclusions

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A model proposed in another publication¹⁾ for steady state uni-directional solidification is evolved to a relationship between solidification variables and dendrite structure/morphology in non-steady state directional solidification. Dendrite structure and inclusion behaviors in columnar zone of continuous cast slabs are discussed with the model.

Behaviors of inclusions in calcium-treated clean steels are discussed based on equilibrium considerations as well as widely accepted results and knowledges hitherto. An idea is introduced to interpret competitive precipitations of oxides and sulfides for calcium in residual melts between dendrite arms where the inclusions precipitate.

Quantitative predictions are enabled with the present model, and several equations are given to volume fraction, size and morphology of the inclusions in calcium-treated clean steels in relation with Ca–S–O balance and solidification variables.

KEY WORDS: sulfide shape control; calcium treatment; clean steel; directional solidification.

1. Introduction

A numerical treatment of sulfide- and oxide-inclusions in continuous cast slabs of commercially produced clean steels is explained with aid of the results of basic experiments in another publication¹⁾ and equilibrium considerations. Ordinarily these steels are finished by secondary refining process with calcium-treatment, and contain extremely small amount of sulfur and oxygen but medium range of aluminum because of aluminum-killed steel. Dozens of mass-ppm calcium remain in melt consequently. All these participate in the characteristic behaviors of inclusions in the steels. Although the amount of inclusions in the steels is very small, still some properties relating to hydrogen in materials are severely impaired by the inclusions. Therefore, numerical predictions having coherency to experimental results about the inclusions in steel are highly required to control these damages.

In the present report, quantitative descriptions or approximations about sulfide- and oxide-inclusions are thoroughly pursued, based on a model for competitive precipitations of both inclusions for calcium in the residual melt. A concept; Solidification-Unit-Cell: S.U.C.,¹⁾ which is devised for modelling of steady state uni-directional dendrite structure, is developed to treat non-steady state directional dendrite structure. Based on

the extended idea of S.U.C., inclusion model is equipped with several equations consisting of initial compositions of steel and location in CC-slabs.

An example is shown applying the present results to 210 mm-thickness continuous cast slab. Volume fraction, average size, morphology of inclusions are treated. It is understood that the numerical prediction fairly coincides with observations.

2. Experiment

The experiment consists of two subjects. The first deals with a quantitative relationship between dendrite structure in columnar zone of continuous cast slabs (CC-slab) and solidification variables. Here a basic results of steady state uni-directional solidification experiments are evolved to non-steady state directional solidifications. The second subject concerns an evaluation method of the amount of two kinds of sulfides; calcium-sulfide and manganese-sulfide, in terms of Ca–S–O balance of incipient steel melt. A calculating method of oxides are proposed appropriating tentative hypothesis with which oxide behavior in calcium-treated clean steels is well interpreted.

All the sample steels were produced in a unit heat of 250–300 ton with a top-blown basic converter, successively de-gassed with RH-process and finally calcium-

treated in injection process. Most of the heats were cast in 210 mm-thickness continuous cast slab machine, but some were up-hill poured into 38-ton ingots.

3. Results

3.1. Dendrite Structure in Columnar Zone of CC-slab

The chemical composition of a sample steel with which dendrite structure was investigated is shown in Table 1. The data of dendrite observed were listed in Table 2. Dendrite arm spacings in Table 2 are measured in columnar zone of the 210 mm-thickness CC-slab in terms of distance from slab surface. In Table 2 calculated values for R : travel velocity of solidification front and G : temperature gradient around solid/liquid zone are

Table 1. Composition of CC-slab used for observation of dendrite structure. (mass%)

C	Si	Mn	P	S	V	Al	N	O
0.18	0.35	1.43	0.020	0.005	0.05	0.027	0.0044	0.0021

Table 2. Dendrite arm spacings measured in columnar zone of CC-slab. (Table 1)

Distance from surface: D_s (mm)	λ_1 (μm)	λ_2 (μm)	R ($\mu\text{m/s}$)	G ($^{\circ}\text{C/mm}$)	$R^{-0.14}G^{-0.50}$ (R : $\mu\text{m/s}$, G : $^{\circ}\text{C/mm}$)
1.5	55	26	4090	129	0.0269
3.5	128	51	1750	55.1	0.0464
6.5	145	57	943	29.7	0.0691
11.5	163	64	533	16.8	0.0997
21.5	174	85	285	8.98	0.149
41.5	273	128	148	4.65	0.228

added. The calculation method will be explained in the following discussion.

3.2. Observation of Inclusions and Chemical Analysis

The chemical compositions of 16 heats of sample steels which were submitted to inclusion analysis fall in the range shown in Table 3. All the steels were produced commercially as linepipe material of API5LX-X65 grade. Some of the 16 heats were up-hill poured into an ingot of 38 ton unit weight. They were used to analyze oxygen partition into calcium-compounds and non-calcium ones, based on equilibrium considerations. Sulfur partition was calculated from oxygen partition as will be discussed below.

The chemical analysis was done with scraped chips from columnar zone of the slab or the ingots where no serious influence of either melt-convection or sedimentation of equiaxed flocks is recognized. From the same portion samples for inclusion analysis were taken and $[\% \text{Ca}]_{\text{as CaO}}$, calcium concentration as constituent of calcium-oxide extracted with organic solvent extraction method, was analyzed and shown in Table 4. $[\% \text{Ca}]_{\text{as CaS}}$ is calculated as a difference between the total calcium concentration in inclusion and the above obtained measured value: $[\% \text{Ca}]_{\text{as CaO}}$. Since the total amount of calcium: $[\% \text{Ca}]_0$ in chemical analysis and that in inclusion analysis are not always equal, the data of calcium in Table 4 are not consistent. The discrepancy was normalized in the following discussions on inclusions.

The observations of inclusions were done in rolled plates. Instead of volume fraction, total length of specified inclusions in a unit area is measured. Length

Table 3. Chemical compositions of mill-processed aluminum-killed clean steels.

C mass%	Si →	Mn →	P →	S ppm	Ni %	Mo →	Nb →	V →	Ti →	Al →	N ppm	O →	Ca →
0.03– 0.05	0.30– 0.32	1.39– 1.61	0.009– 0.017	19– 29	0.17– 0.20	0.16– 0.21	0.04	0.06– 0.07	0.01– 0.02	0.020– 0.034	48– 62	24– 34	0– 50

Table 4. Chemical analysis of sulfide- and oxide-inclusions.

Steel	Chemical analysis (mass%)			Inclusion analysis (mass%)		Calculated value	
	$[\% \text{S}]_0$	$[\% \text{O}]_0$	$[\% \text{Ca}]_0$	$[\% \text{Ca}]_{\text{as CaO}}$	$[\% \text{Ca}]_{\text{as CaS}}$	$[\% \text{Ca}]_0/[\% \text{O}]_0$	$[\% \text{Ca}]_0/[\% \text{S}]_0$
I- 1	0.0016	0.0016	0.014	0.0005	0.0016	0.875	0.875
2	18	18	17	5	20	0.944	0.944
3	18	31	24	4	14	0.774	1.38
4	26	51	47	11	26	0.922	1.81
5	32	56	56	20	31	1.00	1.75
6	28	17	23	4	16	1.35	0.821
7	28	27	25	5	16	0.926	0.893
8	37	47	44	13	26	0.936	1.19
9	24	16	30	8	17	1.88	1.25
10	27	25	36	11	24	1.44	1.33
11	45	54	91	23	40	1.69	2.02
12	13	26	24	12	14	0.923	1.85
13	16	28	37	18	20	1.32	2.31
14	16	40	43	17	19	1.08	2.69
15	18	38	42	23	18	1.11	2.33
16	20	20	24	6	19	1.20	1.20

Table 5. Calculated volume fractions and the observed results (Steels in Table 3, SPC, OPC and chemical analysis data are reproduced from Tables 4 and 6).

Steel	[%S] ₀ × 10 ⁻⁴	SPC	<i>f_V</i> (MnS) × 10 ⁻⁵	[%O] ₀ × 10 ⁻⁴	OPC	<i>F</i> _{ox}	<i>f_V</i> (Al ₂ O ₃) × 10 ⁻⁵	<i>f_L</i> (MnS)	<i>f_L</i> (B-Type)
I- 1	16	0.578	3.58	16	0.0613	0.169	5.58	0.089	0.12
2	18	0.613	3.69	18	0.0713	0.196	6.08	0.16	0.075
3	18	0.799	1.92	31	0.0855	0.235	9.96	0.0095	0.23
4	26	0.924	1.05	51	0.134	0.371	14.3	0.0071	0.23
5	32	0.910	1.53	56	0.140	0.385	14.5	0.34	0.15
6	28	0.549	6.69	17	0.0888	0.244	5.40	0.072	0.099
7	28	0.587	6.13	27	0.0663	0.182	9.28	0.069	0.054
8	37	0.725	5.39	47	0.089	0.245	14.9	0.15	0.31
9	24	0.750	3.18	16	0.188	0.517	3.25	0.062	0.072
10	27	0.781	3.13	25	0.153	0.421	6.08	0.070	0.13
11	45	0.963	0.882	54	0.273	0.751	5.65	0.068	0.094
12	13	0.932	0.469	26	0.137	0.377	6.80	0.0065	0.075
13	16	0.994	0.051	28	0.244	0.671	3.87	0.00072	0.11
14	16	0.994	0.051	40	0.233	0.641	6.03	0.00085	0.18
15	18	0.995	0.048	38	0.207	0.569	6.88	0.00050	0.087
16	20	0.730	2.86	20	0.115	0.316	5.75	0.038	0.15

cf. $f_L(\text{MnS}) = \sum l_{i\text{MnS}}/25$, $f_L(\text{B-Type}) = \sum l_{i\text{B-Type}}/25$

ratio of manganese-sulfide, for instance, is defined as $f_L(\text{MnS}) = \sum l_{i\text{MnS}}/25$, where $\sum l_{i\text{MnS}}$ is a sum of lengths of all manganese-sulfide inclusions observed in a rectangle: (columnar zone thickness in rolled plate) × (25 mm in rolling direction), $f_L(\text{Al}_2\text{O}_3)$ and $f_L(\text{B-Type})$ are calculated in the same manner for elongated cluster-like alumina inclusions and calcium-aluminate ones, respectively. They are listed in Table 5.

4. Discussion

4.1. Solidification Variables in Continuous Cast Slabs

What we know about solidification variables in CC-slabs under operation is either results of computer-calculation based on the classical heat transfer equation with finite difference or finite element method²⁻⁴⁾ or direct data of solid shell thickness using copper pins⁵⁾ or tracer.⁶⁻⁷⁾ Solidification variables, R and G , are not given directly from these results but have to be calculated assuming T_L and T_S to the appropriate locations. A well known result about solid-shell growth in a continuous cast slab is expressed with a parabolic function³⁾;

$$Ds = (\text{constant}) \times \sqrt{t} \quad \text{.....(1)}$$

where, Ds : thickness of solid-shell at time t , t : duration of time after a concerned portion passed meniscus. For the manufacturing condition with which the present steels were cast, Eq. (1) is expressed as follows;

$$H_L(\text{mm}) = 3.7\sqrt{t} \quad (t: \text{s}) \quad \text{.....(2)}$$

$$H_S(\text{mm}) = 3.3\sqrt{t} \quad (t: \text{s}) \quad \text{.....(3)}$$

where, H_L and H_S represent the distance between slab surface and a point of liquidus: T_L and that of solidus: T_S , respectively. Taking $Ds = (H_L + H_S)/2$, R is obtained.

$$R[\mu\text{m/s}] = dDs/dt = 6130/Ds \quad (Ds: \text{mm}) \quad \text{.....(4)}$$

and G can be calculated as,

$$G[^\circ\text{C/mm}] = (T_L - T_S)/(H_L - H_S) = 193/Ds \quad (Ds: \text{mm}) \quad \text{.....(5)}$$

where T_L and T_S are given as 1513 and 1491°C, respectively.

4.2. Dendrite Structure in Columnar Zone of CC-slabs and Solidification Variables

The dendritic solidification in columnar zone of CC-slabs can be regarded as a stepwise succession of localized steady state uni-directional solidifications, since it is widely accepted that the increase in arm spacings at any location in columnar zone is correlated with local solidification time.^{8,9)} This means, primary dendrite arm spacing, λ_1 , secondary arm spacing, λ_2 and the volume of S.U.C., V_{SUC} at any location in the columnar zone are related to localized solidification parameter: $R^{-m}G^{-n}$. Using the relationships between λ_1 , λ_2 , V_{SUC} and R , G derived from the steady state uni-directional solidification analysis,¹⁾

$$\lambda_1 = 1750R^{-0.14}G^{-0.50}, \quad \lambda_2 = 870R^{-0.14}G^{-0.50} \quad \text{..(6)}$$

$$V_{\text{SUC}} = \lambda_1^2 \cdot \lambda_2 = 2.7 \times 10^9 R^{-0.42} G^{-1.5} \quad \text{.....(7)}$$

where λ_1 and λ_2 in μm , V_{SUC} in μm^3 , R in $\mu\text{m/s}$, G in $^\circ\text{C/mm}$. Inserting Eqs. (4) and (5) into Eq. (6),

$$\lambda_1[\mu\text{m}] = 36 \cdot Ds^{0.64} \quad (Ds: \text{mm}) \quad \text{.....(8)}$$

$$\lambda_2[\mu\text{m}] = 18 \cdot Ds^{0.64} \quad (Ds: \text{mm}) \quad \text{.....(9)}$$

are derived.

The figures obtained from the observation are slightly deviating from the correlation between arm spacings and Ds given by Eqs. (8) and (9) as shown in Fig. 1, however, these equations can provide not so bad approximation of the actual data as seen in Fig. 1.

4.3. Model of Dendrite Aggregates for Directional Solidification

Based on the model¹⁾ of dendrite aggregates in steady state uni-directional solidification, the most simple mod-

Fig. 1. Correlation between observed λ_1/λ_2 and D_s , relationships calculated by Eqs. (8) and (9) are shown together.

Fig. 2. A model for Solidification-Unit-Cell stack of a primary dendrite in non-steady state directional solidification.

el for directional solidification is magnifying 14-facet polyhedrons along with primary arm direction as illustrated in Fig. 2. According to the model, the volume of S.U.C.: V_{SUC} is given from Eqs. (7), (8) and (9),

$$V_{\text{SUC}} = \lambda_1^2 \cdot \lambda_2 = 2.4 \times 10^4 D_s^{1.9} \quad (V_{\text{SUC}}: \mu\text{m}^3, D_s: \text{mm}) \quad \dots (10)$$

and the number of nodes per unit volume: A_p is given,

$$A_p = 6/V_{\text{SUC}} = 2.5 \times 10^{-4} D_s^{-1.9} \quad (A_p: \text{number}/\mu\text{m}^3, D_s: \text{mm}) \quad \dots (11)$$

since one apex of a 14-facet polyhedron in Fig. 2 is shared by four adjacent polyhedrons. The relations of V_{SUC} and A_p to D_s are shown in Fig. 3.

The real dendrite structure in columnar zone of CC-slabs is, however, different from that depicted with the model in Fig. 2. As a model for the structure it has to include various length of primary arms as illustrated in Fig. 4. If some idea like S.U.C. shall be introduced, we have to abandon a requirement for continuity of each primary arm, or a regularity of the structure, as un-

Fig. 3. Dependency of V_{SUC} and A_p upon D_s .

Fig. 4. Illustration of dendrite structure in columnar zone of CC-slab.

Fig. 5. A model for enclosure by preferential dendrite arms in non-steady state directional solidification.

derstood from Fig. 5, i.e., before two prevailing arms become in contact, the rest of the primary arms are blocked and enclosed in between. During the process, the residual melt, especially, location: A and B in Fig. 5 play the same role as that of Solute-Enriched-Node: S.E.N.¹⁾ in steady state uni-directional solidification, especially as preferential site for inclusion precipitation than any other. And it is reasonable to postulate that density of such most enriched locations is correlated to A_p given by Eq. (11).

Fig. 6. Correlation between $OPC_{incl.}$ and $[\%Ca]_0/[\%O]_0$.

4.4. Partition of Oxygen into Calcium-oxide and Other-oxides in Aluminum-killed Clean Steel

Solute oxygen in melt of aluminum-killed clean steel is fixed as oxide inclusions in solid, and solute oxygen in the solid is negligibly small. If calcium is added in the melt, the oxides are calcium-oxide, aluminum-oxide and small amount of silicon-oxide. These three oxides often co-exist when calcium content is not high enough and proper amount of aluminum is added.¹⁰⁾ But in case of calcium content higher than around 5–10 mass-ppm, calcium-oxide tends to be free from others, and in extreme case, *i.e.*, calcium content exceeds a couple of ten mass-ppm, isolated inclusions of CaO-phase appear.

Oxygen in such solid steel is therefore deemed partly as oxygen as CaO, partly as oxygen as alumina-silicate;

$$[O]_0 \sim [O]_{as\ CaO} + [O]_{as\ Alumina-Silicate} \quad (12)$$

where $[O]_0$ indicates the atomic concentration of solute oxygen in an incipient steel melt just before solidification start and the right hand terms express the amount of oxygen in the inclusions precipitating in a unit mass of solid steel, assuming macro-segregations of the elements during solidification as negligible. The ratio defined by Eq. (13) is named as Oxygen-Partition-Coefficient: OPC;

$$OPC = [O]_{as\ CaO} / [O]_0 \quad (13)$$

OPC represents quasi an efficiency of calcium as suppressor against alumina-silicates. OPC is expected to have a correlation with $[Ca]_0/[O]_0$, since $[O]_{as\ CaO}$ in Eq. (13) is equal to $[Ca]_{as\ CaO}$ from the stoichiometry of $[Ca]-[O]$ in CaO-inclusion. But this is not verified with the data in Table 4 as shown in Fig. 6. One of the reasons is calcium reacts not only on oxygen but on sulfur simultaneously.

4.5. Partition of Sulfur into Calcium-sulfide and Manganese-sulfide

Behavior of sulfur in aluminum-killed clean steel is similar to that of oxygen in such manner that most of solute sulfur in steel-melt precipitates as sulfides. In calcium-treated steel the sulfides are principally calcium-sulfide and manganese-sulfide. Neglecting concentration

Fig. 7. Correlation between $SPC_{incl.}$ and $[\%Ca]_0/[\%S]_0$.

of solute sulfur in solid steel, similar relation for sulfur as the one expressed with Eq. (12) for oxygen:

$$[S]_0 \sim [S]_{as\ CaS} + [S]_{as\ MnS} \quad (14)$$

is derived.

The ratio: $[S]_{as\ CaS}/[S]_0$ is again an efficiency of calcium reducing manganese-sulfide, and is named as Sulfur-Partition-Coefficient: SPC;

$$SPC = [S]_{as\ CaS} / [S]_0 \quad (15)$$

SPC has not close correlation with $[Ca]_0/[S]_0$ either, as shown in Fig. 7 which is plotted from the data in Table 4.

These estrangements shown in Figs. 6 and 7 suggest that the effort to draw a simple relationship between Ca-S-O balance in melt and behaviors of oxides and sulfide in solid would be in vain. The faults are,

(1) the inclusions precipitate among the dendrite arms in final solidification process of the whole system, not in free melt-mass,

(2) the composition of residual melt where the inclusions precipitate is different significantly from that of incipient melt,

(3) the precipitation of oxide and that of sulfide are not independent, but are closely influenced mutually, and any precipitation of the inclusions reduces the calcium concentration in the residual melt to an extent which could not be neglected, because volume of residual melt is small enough at the instance. Regarding to the above pointing (3), it is important to know the partition of calcium into sulfide and oxide.

4.6. Dendritic Segregation and Oxide- and Sulfide-inclusions in Residual Melt

During a dendritic solidification solute elements, *e.g.*, Ca, S, O, *etc.*, are ejected into residual melt, and are enriched there. For a S.U.C. with fraction of solid: f , the following relations

$$\begin{aligned} [Ca]_{s(f)} / [Ca]_{L(f)} &= k_{Ca}^f \\ [S]_{s(f)} / [S]_{L(f)} &= k_S^f \\ [O]_{s(f)} / [O]_{L(f)} &= k_O^f \end{aligned} \quad (16)$$

can be applied between solid, or surface layer of dendrite arms, and liquid, or residual melt close to the interface. Where $[X]_{s(f)}$ and $[X]_{L(f)}$ indicate the concentration of element X in the surface layer and that of the residual

melt, respectively, and k_X^f is a distribution coefficient of element X between solid and liquid at the temperature corresponding to f . Providing that (1) no convection occurs in melt steel, and (2) enriched elements are given enough time to diffuse in the solid and the melt, the following equation:

$$[X]_0 \cdot V_{\text{SUC}} = [X]_{\text{SUC}} \cdot V_{\text{SUC}} \cdot f + [X]_{\text{LUC}} \cdot V_{\text{SUC}} \cdot (1-f)$$

can be assumed.

Inserting Eq. (16) into the equation above,

$$\begin{aligned} [Ca]_{\text{LUC}} &= [Ca]_0 / (fk_{\text{Ca}}^f + 1 - f) \\ [S]_{\text{LUC}} &= [S]_0 / (fk_{\text{S}}^f + 1 - f) \dots\dots\dots(17) \\ [O]_{\text{LUC}} &= [O]_0 / (fk_{\text{O}}^f + 1 - f) \end{aligned}$$

are derived.

If each or both of the following equations is/are satisfied, either/both of calcium-sulfide and calcium-oxide precipitate(s) in the residual melt.

$$\begin{aligned} L_{\text{CaS}}^f &= [Ca]_{\text{LUC}} \cdot [S]_{\text{LUC}} \\ &= [Ca]_0 \cdot [S]_0 / \{(fk_{\text{Ca}}^f + 1 - f)(fk_{\text{S}}^f + 1 - f)\} \\ L_{\text{CaO}}^f &= [Ca]_{\text{LUC}} \cdot [O]_{\text{LUC}} \\ &= [Ca]_0 \cdot [O]_0 / \{(fk_{\text{Ca}}^f + 1 - f)(fk_{\text{O}}^f + 1 - f)\} \end{aligned}$$

where L_{CaS}^f and L_{CaO}^f are solubility products of CaS and CaO, respectively, at the temperature corresponding to f . It should be noted the solubility product: L_{CaS}^f and L_{CaO}^f are for the residual melt of a S.U.C. with fraction of solid: f . In general, solubility product decreases with reduction of temperature, or increase in f . **Figure 8** depicts all these behaviors. Increase in f brings about

Fig. 8. Interpretation on microsegregation in residual melt (Sulfur-Enriched-Network/Node) and precipitation/growth of inclusions therein.

enrichment of Ca, S, O in the residual melt, and concentration product: $[Ca]_{\text{LUC}} \cdot [O]_{\text{LUC}}$ reaches L_{CaO}^f , which causes precipitation start of CaO inclusion, resulting in reduction of $[Ca]_{\text{LUC}+df} \cdot [O]_{\text{LUC}+df}$ along the solubility line.

Let $[\xi]$ be the molar amount of CaO-inclusion precipitating in the S.U.C. during the interval between f and $f+df$, the following equation is led, since the precipitated inclusion conserves stoichiometry, i.e.,

$$\begin{aligned} [CaO]_{\text{as ppt}} &= [Ca]_{\text{as CaO}} = [O]_{\text{as CaO}} = [\xi], \quad L_{\text{CaO}}^{f+df} = \\ [Ca]_{\text{LUC}+df} \cdot [O]_{\text{LUC}+df} &= ([Ca]_{\text{LUC}} - [\xi]) \cdot ([O]_{\text{LUC}} - [\xi]). \end{aligned}$$

The quadratic equation of $[\xi]$ is reduced to as follows, since the relations: $[Ca]_{\text{LUC}} \cdot [O]_{\text{LUC}} = L_{\text{CaO}}^f$, and $L_{\text{CaO}}^f \sim L_{\text{CaO}}^{f+df}$,

$$([\xi])^2 - \{[Ca]_{\text{LUC}} + [O]_{\text{LUC}}\} ([\xi]) = 0$$

and

$$\begin{aligned} ([\xi]) &= [Ca]_{\text{LUC}} + [O]_{\text{LUC}} \\ &= [Ca]_0 / (fk_{\text{Ca}}^f + 1 - f) + [O]_0 / (fk_{\text{O}}^f + 1 - f) \end{aligned}$$

therefore,

$$\begin{aligned} [O]_{\text{as CaO}} / [O]_0 &= [\xi] / [O]_0 \\ &= [Ca]_0 / \{[O]_0 (fk_{\text{Ca}}^f + 1 - f)\} + 1 / (fk_{\text{O}}^f + 1 - f) \dots(18) \end{aligned}$$

The same equation can be introduced for CaS.

$$\begin{aligned} [S]_{\text{as CaS}} / [S]_0 &= [Ca]_0 / \{[S]_0 (fk_{\text{Ca}}^f + 1 - f)\} \\ &+ 1 / (fk_{\text{S}}^f + 1 - f) \dots\dots\dots(19) \end{aligned}$$

It is clear the integrations of Eqs. (18) and (19) give OPC and SPC, respectively. But the integration must be done altogether, because calcium in the residual melt reacts on oxygen and sulfur as depicted in **Fig. 8**:

$$\begin{aligned} \text{OPC} + \text{SPC} &= \int \{ [O]_{\text{as CaO}} / [O]_0 + [S]_{\text{as CaS}} / [S]_0 \} df \\ &= \text{Function} ([Ca]_0 / [O]_0, [Ca]_0 / [S]_0) \dots\dots\dots(20) \end{aligned}$$

Another important relation has to be introduced to

Fig. 9. Relationship between OPC and $(16/40)([\%Ca]_0/[\%O]_0)(32/40)([\%Ca]_0/[\%S]_0)$.

Table 6. Comparison between chemical analysis and calculated values for OPC/SPC.

Steel	Calculated value from analyses (Table 4)				Calculated values	
	(mass%)		OPC =	SPC =	OPC* ¹	SPC* ²
	[%O] _{as CaO}	[%S] _{as CaS}	$\frac{[\%O]_{as CaO}}{[\%O]_0}$	$\frac{[\%S]_{as CaS}}{[\%S]_0}$		
I- 1	0.00013	0.00085	0.081	0.53	0.0613	0.578
2	14	109	0.078	0.61	0.0713	0.613
3	21	149	0.068	0.83	0.0855	0.799
4	56	264	0.11	(1)	0.134	0.924
5	88	272	0.16	0.85	0.140	0.910
6	18	147	0.11	0.53	0.0888	0.549
7	24	152	0.089	0.54	0.0663	0.587
8	59	235	0.13	0.64	0.089	0.725
9	38	163	0.24	0.68	0.188	0.750
10	45	197	0.18	0.73	0.153	0.781
11	133	462	0.25	(1)	0.273	0.963
12	44	103	0.17	0.79	0.137	0.932
13	70	156	0.25	0.98	0.244	0.994
14	81	182	0.20	(1)	0.233	0.994
15	94	148	0.25	0.82	0.207	0.995
16	23	145	0.12	0.73	0.115	0.730

*¹ OPC = 0.08([%Ca]₀/[%O]₀)([%Ca]₀/[%S]₀)

*² SPC = 0.8([%Ca]₀/[%S]₀) - 0.16([%Ca]₀/[%S]₀)²

solve OPC and SPC. That is an equation concerning the partition of calcium into oxide and sulfide, regarding solute calcium in solid steel to be practically negligible¹⁰⁾,

$$\begin{aligned} [Ca]_0 &= [Ca]_{as CaO} + [Ca]_{as CaS} \\ &= [O]_{as CaO} + [S]_{as CaS} \quad \dots\dots\dots(21) \\ &= [O]_{as CaO} + [S]_0 \cdot SPC \end{aligned}$$

dividing Eq. (21) by [O]₀,

$$([Ca]_0/[O]_0) = OPC + ([S]_0/[O]_0) \cdot SPC \quad \dots\dots\dots(22)$$

The analytical solution of simultaneous Eqs. (20) and (22) seems to be still ambiguous, because integration of Eq. (20) requires rather rough estimations to k_{Ca} , k_S , k_O .

In the present study, therefore, a trial-and-error approach was taken, considering that the solutions of the simultaneous Eqs. (20) and (22), or OPC and SPC, should have two explicit constants: $[Ca]_0/[O]_0$ and $[Ca]_0/[S]_0$, and a nice correlation between OPC and $([Ca]_0/[O]_0) \times ([Ca]_0/[S]_0)$ was found as shown in Fig. 9. The correlation is expressed as,

$$\begin{aligned} OPC &= 0.25([Ca]_0/[O]_0)([Ca]_0/[S]_0) \\ &= 0.08([\%Ca]_0/[\%O]_0)([\%Ca]_0/[\%S]_0) \quad \dots(23) \end{aligned}$$

Inserting OPC into Eq. (22), SPC is given as,

$$\begin{aligned} SPC &= ([Ca]_0/[S]_0) - ([O]_0/[S]_0) \cdot OPC \\ &= 0.8([\%Ca]_0/[\%S]_0) - 0.16([\%Ca]_0/[\%S]_0)^2 \quad \dots\dots\dots(24) \end{aligned}$$

The correlation given by Eq. (24) exhibits a fairly good fitting with the observed data in Table 6 as shown in Fig. 10.

4.7. Volume Fraction and Size of Sulfide Inclusions

Under the approximation expressed with Eq. (24), volume fraction of manganese-sulfide inclusion: $f_V(\text{MnS})$

Fig. 10. Relationship between calculated SPC and measured one.

is calculated with additional premises (1) and (2) in Appendix, and Eq. (25) is obtained. Figure 11 shows a correlation between the observed data: $f_L(\text{MnS})$ in Table 5 and $f_V(\text{MnS})$ by Eq. (25). Inserting Eq. (10) into the equation in premise (2), another numerical relationship: Eq. (26) between inclusion size and slab site is also obtained.

$$f_V(\text{MnS}) = 0.053[\%S]_0(1 - SPC) \quad \dots\dots\dots(25)$$

$$d_{\text{MnS}}[\mu\text{m}] = -6.84 + 7.3 \log Ds \quad (Ds: \text{mm}) \quad \dots\dots(26)$$

Since morphology of manganese-sulfide inclusion in the present steels is dendritic as illustrated in Fig. 12, the d_{MnS} gives a mean rod-diameter of dendritic branches. The overall stretch size of an inclusion is unable to be calculated, therefore only a radius of a sphere which has an equivalent volume to an inclusion can be obtained,

provided the number of sites where inclusions are located is equal to $\eta \cdot Ap$, where Ap is given by Eq. (11) and η is constant. Take η as unity, r_{MnS} : radius of the equivalent volume sphere, Eq. (27) is derived.

Fig. 11. Correlation between $f_v(\text{MnS})$ and $f_L(\text{MnS})$.

Fig. 12. Calculated diameter by Eq. (27) for equivalent sphere to MnS-inclusion volume in comparison with MnS-dendrite arm diameter by Eq. (26). 210 mm-thickness CC slab with 0.18%C–1.43%Mn–0.0030%S–0.025%O–(0–0.0065)%Ca, Al-killed steel. ① Ca: 0%, ② 0.0025%, ③ 0.0035%, ④ 0.0055%, ⑤ 0.0065%

OPC	Impurities in steel (mass ppm)			Inclusions 20 μm
	Ca	O	S	
0	—	30	25	
0.153	36	25	27	
0.273	35	24	15	
0.395	33	20	11	

Fig. 13. Morphology of oxide-inclusions in calcium-treated clean steel.

$$r_{\text{MnS}}[\mu\text{m}] = \{3f_V(\text{MnS})/4\pi Ap\}^{1/3} \sim 3.7\{[\%S]_0(1-\text{SPC})\}^{0.33} D_s^{0.64} \quad \dots\dots\dots(27)$$

These calculations are applied to a typical clean steel containing different calcium contents and diameter of equivalent sphere: $2r_{\text{MnS}}$ and that of rod: d_{MnS} are calculated and shown in Fig. 12. It should be noted that both diameters: $2r_{\text{MnS}}$ and d_{MnS} increase with increment of D_s , but each dependency on D_s is different. $2r_{\text{MnS}}$: diameter of equivalent sphere (Fig. 12) depends on the amount of manganese and sulfur in one pool of S.E.N., hence free-sulfur content in steel melt and size of steel-dendrite structures. This is the reason for the dependency on calcium contents and D_s (Fig. 12), while d_{MnS} is controlled by a localized solidification parameter: $R^{-m}G^{-n}$, therefore depends only on D_s regardless of calcium concentration.

4.8. Hypothesis of Oxide-inclusions in Clean Steel

Oxygen in calcium-treated aluminum-killed clean steel is deemed to be fixed practically as either calcium-oxide or aluminum-oxide, since amount of silicon-oxide is quite small. These two oxides generally form mixed phase inclusions: $m\text{CaO} \cdot n\text{Al}_2\text{O}_3$ ranging from Al_2O_3 to CaO depending on activity balance of mainly Ca-Al in the steel.

It is well known that binary oxides: $m\text{CaO} \cdot n\text{Al}_2\text{O}_3$ exhibit the minimum melting point at m/n around 12/7, and some previous works^{11,12)} showed the data from which the morphology of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is regarded as spherical. In the present study morphology of $m\text{CaO} \cdot n\text{Al}_2\text{O}_3$ is observed in rolled plates and the correlation with OPC-value was carefully examined. The result was shown in Fig. 13. The morphology of calcium-aluminate inclusions in steels with lower OPC-value than approximately 0.2 shows a co-existing state of elongated small fragments (so-called B-type) and spherical form (C-type). The fraction of spherical inclusions increases with increment of OPC-value, and in steels to which OPC-value is calculated as around 0.3 and higher, the morphology of inclusions is a blocky mixture as Haida *et al.*¹¹⁾ and Salter and Pickering¹²⁾ showed. And for higher OPC-value it was anticipated that inclusions become again elongated massive fragments although sufficient evidence was not obtained.

From the present results of observation, following hypothesis was tentatively made, considering the preceding works of Salter and Pickering¹²⁾ and Steinmetz and Lindenberg.^{13,14)} [HYPOTHESIS] Steels with a Ca-S-O balance corresponding to OPC-value: 0.364 contain solely $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ -inclusion, and in case of OPC less than 0.364, oxide inclusions consist of spherical calcium-aluminate ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) and dendritic/eutectic oxides. Based on the hypothesis above, a model for oxide inclusions in calcium-treated steels is proposed. Denote F_{OX} as $[\text{O}]_{\text{as } 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3}/[\text{O}]_0$ which can be deemed as an index for spherical oxides, then Eq. (28) is derived from stoichiometry of calcium-aluminate, again with the premises as follows; 1) oxide phase in the oxides is either/both of CaO and Al_2O_3 , and other oxides

Fig. 14. Concept for oxide shape control factor; F_{OX} and OPC.

Fig. 15. Correlation between $f_V(\text{Al}_2\text{O}_3)$ and $f_L(\text{Al}_2\text{O}_3)$.

are negligibly few, 2) solute oxygen in solid steel is little enough, 3) rate of $[\text{O}]_{\text{as dendritic oxides}}/[\text{O}]_{\text{as } 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3}$ is proportional to $(1-F_{\text{OX}})/F_{\text{OX}}$ for steels with OPC equal to and less than 0.364 as depicted in Fig. 14. For steels with higher OPC-value no model can be made from the present experiment.

$$F_{\text{OX}} = [\text{O}]_{\text{as } 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3}/[\text{O}]_0 = 2.75 \cdot \text{OPC} \quad \dots\dots(28)$$

With the premises 1), 2) and 3), volume fraction of Al_2O_3 -inclusion can be calculated for steel of Ca-S-O balance: $\text{OPC} \leq 0.364$ as follows,

$$\begin{aligned} f_V(\text{Al}_2\text{O}_3) &= ([\text{Al}_2\text{O}_3]/3[\text{O}])(\rho_{\text{Steel}}/\rho_{\text{Al}_2\text{O}_3})[\%O]_{\text{as Al}_2\text{O}_3}/100 \\ &= 0.042[\%O]_0(1-F_{\text{OX}}) \quad \dots\dots\dots(29) \end{aligned}$$

The correlation between lineal fraction of oxides: $f_L(\text{Al}_2\text{O}_3)$ and calculated volume fraction: $f_V(\text{Al}_2\text{O}_3)$ by Eq. (29) is shown in Fig. 15. The countable length of an elongated oxide is prescribed as «a length of one elongated cluster of fragments comprising not less than three pieces which do not separate from each adjacent piece with not more than $25\text{ }\mu\text{m}$ interval in length direction». Although the correlation in Fig. 15 between calculated $f_V(\text{Al}_2\text{O}_3)$ and observed $f_L(\text{Al}_2\text{O}_3)$ is not so nice as manganese-sulfide in Fig. 11, it can be still considered that Eq. (29), hence the discussion here with a tentative hypothesis, provides a useful quantitative evaluations of oxides in calcium-treated clean steels.

5. Conclusions

Based on a steady state uni-directional solidification model proposed by the present author,¹⁾ a quantitative model is proposed to describe a relationship between dendrite structures in columnar zone of CC-slabs and distance from slab surface. Arm spacings of dendrites in the columnar zone are approximated, applying the relationship between arm-spacing and solidification variables of steady state uni-directional dendritic solidification. The mode of primary dendrites in columnar zone was regarded as a step-wise succession of localized steady state uni-directional ones, and solidification variables such as R and G were calculated from the solid shell model established as the parabolic law.

Quantitative prediction for inclusions in CC-slabs of calcium-treated clean steel was discussed taking thermodynamic equilibrium approaches into account. In the discussion an idea of competitive reaction of oxygen and sulfur for calcium in residual melt among dendrite arms is proposed with the aid of the above evolved dendrite model. The calculated results of volume fraction, size and morphology of sulfide- and oxide-inclusions at given locations in CC-slab are in good coincidence with the observations.

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Appendix

(1) sulfur expressed with $[\text{S}]_{\text{as MnS}}$ in Eq. (14) forms manganese-sulfide inclusion, and the manganese-sulfide inclusion is regarded as pure MnS, i.e., $\rho_{\text{MnS}} = 4.0\text{ g/cm}^3$, and matrix steel $\rho_{\text{steel}} = 7.8\text{ g/cm}^3$,

(2) manganese-sulfides precipitate and solidify between dendrite arms resulting in dendritic II-type morphology with rod diameter: d_{MnS} which is related to solidification parameter as affirmed experimentally¹⁾; $d_{\text{MnS}} = -23.5 + 3.8 \log V_{\text{SUC}}$.

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