Behaviors of Manganese–Sulfide in Aluminum-killed Steel Solidified Uni-directionally in Steady State — Dendrite Structure and Inclusions

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Morphology, size and distribution of II-type manganese–sulfide are investigated taking steel–dendrite structures into account. Quantitative relationships between solidification conditions and steel–dendrite morphology are discussed first, based on steady state uni-directional solidification experiments. A new idea is proposed as Solidification-Unit-Cell, which is applied to a numerical treatment of relationship between dendritic structure of manganese–sulfide inclusions and solidification conditions. Diameter of dendritic II-type manganese–sulfide rods is correlated to a solidification parameter: $R^{-m}G^{-n}$ which originally is related to steel–dendrite arm spacings, whereas stretches of the inclusions are related to the size and shape of residual melt pool, and amounts of constituent elements supplied thereinto.

KEY WORDS: dendrite; manganese–sulfide; directional solidification; solidification variables.

1. Introduction

Purpose of the present investigation is to formulate a quantitative relationship between solidification variables and size/morphology of manganese–sulfide in directionally solidified aluminum-killed steels with a very low sulfur concentration. These steels are produced through heavy de-sulfurizations commercially. Sulfur concentration in these steels is extremely low, still manganese–sulfide inclusions exist even in columnar zone of continuous cast slabs. Some properties of steel materials are seriously impaired by the inclusions. Amount, size and morphology of these persistently remaining manganese–sulfide are, therefore, of vital interest of pertinent peoples.

This manganese–sulfide is regarded as II-type precipitating in residual melts between dendrite arms in final stage of the overall solidification process, which means consideration on dendritic solidification of steel is indispensable for quantitative description of the manganese–sulfide behavior.

In the present investigation, results of a basic study carried out with steady state uni-directional solidification experiments were explained; relationship between solidification variables and morphology/size/distribution of sulfides, and a modelling of precipitation of manganese–sulfide in residual melts between dendrite arms, in particular, of the final stage, *e.g.*, around the local portion where the concerned system completes solidification.

Particular attention is paid to the difference between size of an overall manganese–sulfide inclusion and diameter of rod cross-section of II-type, or dendritic,

manganese–sulfide. It is shown the latter is simply related to the solidification variables of whole system in direct manner. The former is also controlled by them, but in different manner. Two factors must be taken into account in describing stretch size of a manganese–sulfide inclusion. One is the sulfur concentration in incipient steel melt, the other is unit volume of residual melts from which sulfur and manganese are supplied to the precipitation reaction. This is closely related to steel dendrite arm spacing which is controlled by solidification variables.

An idea of Solidification-Unit-Cell is introduced to explain the above mentioned behavior of manganese sulfide, which gives quantitative descriptions to inclusion models proposed hitherto.

2. Experiment

A series of steady state uni-directional solidification experiments was carried out with an apparatus which Jacobi *et al.* first made for their investigation.¹⁾ This type of apparatus was originated by Chalmers *et al.*, later widely applied to uni-directional solidification study of many alloys, *e.g.*, aluminum–copper alloys.²⁾ The important feature of the present apparatus is able to change G : temperature gradient around solid/liquid zone, practically independent from R : travel velocity of solidification front. Fundamental elements and their assemblage of the apparatus are shown in Fig. 1.

A hollow cylindrical sample; 13 mm-OD, 5 mm-ID, 585 mm-length and 550 g, was put in an alumina pipe;

Fig. 1. Steady state uni-directional solidification apparatus.

Table 1. Chemical composition of steel samples for the steady state uni-directional solidification experiments. (mass%)

Steel	C	Si	Mn	P	S	Al	O	T_L	T_s (°C)
a	0.62	0.12	0.58	0.006	0.073	0.049	0.0011	1490	1423
b	0.52	0.10	0.56	0.003	0.046	0.037	0.0011	1496	1438

14mm-ID, 800mm-length, and was set at a suitable height in the furnace. The sample was heated until an upper half was remelted. The temperature gradients were controlled by electric power supplied to the heater, and by positioning the cylindrical water-cooled copper-shield at suitable heights. Two thermocouples were set at a same height at the beginning, one in the samples was at 460mm height from the sample bottom and another in the furnace atmosphere. When the temperatures reached a steady state temperature higher than the liquidus, the sample started descending at constant velocities, and the temperatures were continuously measured until the thermocouple in sample indicated sufficiently lower temperature than the solidus, and the sample was quench in ice-brine. During the descending of sample, temperature fluctuation of the thermocouple in the atmosphere ranged only $\pm 3^\circ\text{C}$.

The chemical analysis of the sample was shown in Table 1 with liquidus: T_L and solidus: T_s calculated with Turkdogan's formulae³⁾ for the initial chemical compositions. For the time-interval between the thermocouple in sample indicated T_L and quenching, S : descending length of the thermocouple and D : travel distance of solidification front were measured as shown in Fig. 2. Since D was not equal to S , R was calculated from the observation. For the polished sample, the location of T_s at quenching was estimated with descending velocity and the time spent after the thermocouple indicated T_s . G -value was calculated as $(T_L - T_s)/L$, L : distance between solidification front and the location of T_s above

 Geometry when TC shows T_L At quenching

Fig. 2. Change in the relation between solid/liquid and thermocouple in sample.

Table 2. Conditions of the steady state uni-directional solidification experiments.

Test No.	Steel	Max. temp. meas. at melt steel (°C)	Descend velocity (m/h)	($\mu\text{m/s}$)	TC-temp. at quenching (°C)
9	a	1512	0.243	(67.5)	1360
5	a	1535	0.247	(68.5)	1348
3	a	1592	0.246	(68.3)	1342
11	a	1753	0.260	(72.3)	1398
12	b	1535	0.0292	(8.12)	1372
13	b	1605	0.0290	(8.05)	1387
17	b	1736	0.0293	(8.15)	1374

Table 3. Solidification variables of steady state uni-directional solidification.

Test No.	R ($\mu\text{m/s}$)	G (°C/mm)	L (mm)	θ_f (s)	RG (°C/s)
9	28.7	1.99	32.7	1150	0.0570
5	56.2	1.81	36.4	648	0.102
3	28.8	4.81	13.7	474	0.139
11	21.8	16.3	4.04	185	0.356
12	5.28	2.04	28.0	5310	0.0108
13	4.97	4.83	11.8	2360	0.0240
17	4.12	10.9	5.24	1270	0.0449

obtained as shown in Fig. 2. The conditions of each test were listed in Table 2.

3. Results

3.1. Measurement of R and G

A careful analysis of the relation between change in the temperature in sample and the descending length of sample revealed there exists discrepancy between R and the descending velocity of sample. This is schematically interpreted in Fig. 2. The solidification variables thus obtained were shown in Table 3.

3.2. Measurement of Dendrite Arm Spacings

Dendrite arm spacings of primary: λ_1 and secondary: λ_2^f were measured respectively at the fully solidified zone before quenching. The results are shown in Table 4. Also the measurements of secondary arm spacing: λ_2

were done along the solid/liquid zone just before quenching. Results of λ_2 -measurement are shown in Table 5 in terms of distance: D from solidification front. Figure 3 is the typical graphs of each steel. In Fig. 3 temperature curve which the thermocouple in sample indicated at the corresponding position are plotted with the measured one at quenching.

3.3. Observation of Sulfide Inclusions

Sulfide inclusions were observed with photo-microscope. One result of the observations of steel b (Test No. 12) is shown in Fig. 4 as a typical data. At the fully solidified zone before quenching, no iron-sulfide inclusion was observed in samples of steel b (Test Nos. 12, 13, 17). In steel a, same tendency is observed except that iron-sulfide inclusions precipitated at every portion in the samples (Test Nos. 9, 5, 3, 11). In order to get numerical data on volume fraction: f_V , mean diameter of manganese-sulfide rods: d_{MnS} , distribution density per unit volume: N_V , quantitative microscopic measurements were carried out. The data are shown in Fig. 5. The calculation is done under the same assumptions made by Schwerdtfeger⁴⁾ who regarded inclusions as

Table 4. Dendrite arm spacings measured at solidified zone before quenching.

Test No.	λ_1 (μm)	λ_2^f (μm)
9	880-844	316
5	750-683	301
3	480-467	257
11	280-264	172
12	910-909	434
13	690-561	362
17	480-444	228

Table 5. Secondary dendrite arm spacing measured along solid/liquid zone.

λ_2 : Secondary dendrite arm spacing (μm).
 over --- line: D measured from one representative primary dendrite tip.
 under --- line: D measured from averaged level of primary dendrite tips.
 D : Distance from solidification front, L : Length of solid/liquid zone (mm).

Test No. 9 ($L=32.7$)		Test No. 5 ($L=36.4$)		Test No. 3 ($L=13.7$)		Test No. 11 ($L=4.04$)		Test No. 12 ($L=28.0$)		Test No. 13 ($L=11.8$)		Test No. 17 ($L=5.24$)	
D	λ_2	D	λ_2	D	λ_2	D	λ_2	D	λ_2	D	λ_2	D	λ_2
0.1	42.1	—	—	0.2	53	0.2	40.9	0.1	43	0.1	48.5	0.2	71
0.2	47.2	—	—	0.4	68.2	0.5	52.2	0.2	51.1	0.2	55.6	0.5	77
0.4	51.1	2.0	124	0.6	72.3	1.0	50.2	0.4	48.5	0.4	53.2	1.0	105
0.8	57.2	5.0	127	1.0	72.3	1.5	55.9	0.7	58.5	0.7	87.2	1.5	112
1.0	82.9	11.0	130	1.5	73.8	2.0	68.2	1.0	62.9	1.0	96.0	2.0	116
1.5	113	15.0	161	2.0	75.8	2.5	75.7	1.5	53.0	1.5	115	—	—
2.0	106	20.0	150	3.0	96.5	—	—	2.0	60.5	2.0	101	0.5	110
2.5	115	27.0	174	4.0	117	0.5	55.1	3.0	98.5	2.5	142	3.0	135
3.0	120	35.0	181	—	—	1.0	80.8	—	—	—	—	4.0	124
6.0	148	38.5	196	5.0	112	2.0	75.4	0.5	136	1.0	123	6.0	140
—	—	41.0	158	10.0	121	3.0	79.2	5.0	192	2.0	162	6.5	155
1.0	130	42.5	195	15.0	125	5.0	81.8	10.0	183	5.0	201	10.0	214
4.0	155	45.0	182	15.0	123	7.0	115	15.0	242	10.0	204	15.0	228
10.0	144	48.0	192	19.0	137	10.0	130	20.0	249	15.0	218	—	—
19.0	152	65.0	300	20.0	190	15.0	173	30.0	252	20.0	200	—	—
25.0	159	70.0	286	25.0	143	20.0	172	34.0	324	30.0	379	—	—
32.0	187	80.0	317	27.0	140	—	—	70.2	387	40.0	304	—	—
45.0	190	—	—	30.0	339	—	—	74.6	470	50.0	404	—	—
50.0	321	—	—	31.0	151	—	—	80.7	493	—	—	—	—
60.0	362	—	—	38.0	146	—	—	86.7	386	—	—	—	—
70.0	280	—	—	40.0	357	—	—	—	—	—	—	—	—
80.0	306	—	—	50.0	384	—	—	—	—	—	—	—	—
—	—	—	—	65.0	374	—	—	—	—	—	—	—	—

sphere, based on Fullman's theory.⁵⁾

4. Discussion

4.1. Primary Dendrite Arm Spacing: λ_1 and Solidification Variables

It is well known dendrite morphology and dendrite arm spacings are ruled, or controlled by crystallographic

Fig. 3. Increase in secondary dendrite arm spacing; λ_2 in terms of distance from a dendrite tip/solidification front (ave. level of dendrite tips).

Fig. 4. Sulfide inclusions around solidification front and solid/liquid zone after quenching (Test No. 12).

system and solidification conditions. Steels, solidifying primarily either in bcc- or fcc-system, have three preferred orthogonal orientations as Weinberg and Chalmers⁶⁾ pointed out, which is consistent with observations of steel dendrite morphology. Cooling rate (at T_L) at a concerned location: $(dT/dt)_L$, temperature gradient around solid/liquid zone: G , travel velocity of solidification front, or primary dendrite tips: R , local solidification time, or time consumed from liquid to solid at a specified location: θ_f , these physical parameters called solidification variables are closely related to dendrite arm spacing which is the most important index characterizing the structures.

The data of primary arm spacing: λ_1 in Table 4 were better fitted to a parameter: $R^{-m}G^{-n}$ than any other solidification variables, as many preceding research works of uni-directional solidification^{1,2,7-9)} have shown. Applying least squares regression, present data are best fitted to a correlation;

$$\lambda_1 (\mu\text{m}) = 1750 R^{-0.14} G^{-0.50} [R (\mu\text{m/s}), G (^\circ\text{C/mm})] \quad \dots\dots\dots(1)$$

as shown in Fig. 6. The G -exponent: -0.50 falls on average level among the figures ranging -0.3 to -0.7

reported by previous researcher,⁷⁾ and exactly the same value theoretically given by Kurz *et al.*,¹⁰⁾ who derived it based on the Langer-Müller-Krumbhaar proposal¹¹⁾ in which periodicity of sinusoidal thermal fluctuation of solute concentration and temperature, or deviation from unperturbed solid/liquid interface, is deemed to be equal to a radius of the interface capillarity, or dendrite tip radius. In Kurz's theory dendrite arm spacing is calculated taking an ellipsoid-shape dendrite model. On the contrary, R -exponent: -0.14 is somewhat smaller in absolute than any other reported figures as well as the figure: -0.25 given by Kurz *et al.*¹⁰⁾ This might be caused through the measuring method of R , not from the descending velocity but from the corrected value as schematically interpreted in Fig. 2. However, even inserting the figures of descending velocity into R in the least squares, the correlation;

$$\lambda_1 (\mu\text{m}) = 1700 R^{-0.12} G^{-0.47} [R (\mu\text{m/s}), G (^\circ\text{C/mm})] \quad \dots\dots\dots(2)$$

does not approach to the previous works at all. The reason of this is not elucidated within the framework of present study, but the discrepancy between the value

Fig. 5a. Observed results of sulfide inclusions during steady state uni-directional solidification (steel a).

Fig. 5b. Observed results of sulfide inclusions during steady state uni-directional solidification (steel b).

Fig. 6. Relationship between primary dendrite arm spacing and solidification parameter: $R^{-0.14}G^{-0.50}$.

Table 6. Discrepancy in calculated λ_1 -value between R : actual-velocity (Table 3) and R : descending-velocity (Table 2) for 7 tests in Table 2.

Test No.	λ_1 from Eq. (1) R : actual-velocity (μm)	λ_1 from Eq. (2) R : descending-velocity (μm)	λ_1 -value observed (μm)
9	775	742	862
5	733	775	717
3	495	490	474
11	280	274	272
12	966	946	910
13	634	631	626
17	432	430	462

given by Eq. (1) and that by Eq. (2) is within a few percent-point for the experiment range of (R, G) -combination as listed in Table 6. Therefore Eq. (1) is used in the following discussions.

4.2. Secondary Dendrite Arm Spacing: λ_2

The observation of secondary dendrite arm structures shown in Fig. 3 reveals new finding that the linear approximation to the change in λ_2 in terms of distance from solidification front: D is not applicable for the whole solid/liquid zone. Increase in λ_2 near the primary tip follows the exponent relationship: $\lambda_2 = \text{const.} \times D^p$ with $p \sim 0.3$ as previously reported.^{2,7)} But increment rate in λ_2 dulls down first at the location where temperature is a little higher than T_s , and then rises rapidly around the portion of estimated temperature = T_s of the incipient composition as shown in Fig. 3. It should be noted the temperature of the portion where λ_2 reaches to a constant value: λ_2^f is far below the temperature which the thermocouple in sample indicated at quenching. (Figs. 3) Extrapolating the temperature curves in Fig. 3, this temperature is estimated approximately 1300°C, which means vital coarsening and/or coalescence¹²⁻¹³⁾ of secondary dendrite arms commence at just below T_s ($\sim 1340^\circ\text{C}$) and continue until at lower temperatures, presumably, by 100°C or more than T_s . The retardation of completion of solidification is primarily caused by the enrichment of solutes into residual melts between dendrite arms. This phenomenon closely relates to the

Fig. 7. Correlation between λ_1 and λ_2^f .

Fig. 8. Relationship between secondary dendrite arm spacing: λ_2^f and solidification parameter: $R^{-0.14}G^{-0.50}$.

behavior of sulfide inclusions as later discussed.

The measured λ_2^f -values could be also related to solidification parameter: $R^{-m}G^{-n}$ as previous works^{7,14)} reported. However data of λ_2^f in the present investigation are in good correlation with λ_1 as shown in Fig. 7. Based on this, using Eq. (1) for λ_1 , λ_2^f can be approximated as follows.

$$\lambda_2^f (\mu\text{m}) = 0.5\lambda_1 = 870R^{-0.14}G^{-0.50} [R (\mu\text{m/s}), G (^\circ\text{C/mm})] \quad \text{.....(3)}$$

The correlation between solidification parameter and measured λ_2^f is shown in Fig. 8, in which a good fitting is recognized.

It is thought coarsening behavior of secondary arm spacing is an Ostwald-ripening process, hence λ_2 should be correlated to $\log(D/L)$, where, D : distance from primary tips, L : length between the tips and the location where residual melts finally solidify. The value: D/L is naturally a substitute for local solidification time. Indeed this applies within a certain extent of D ($\ll L$), however in locations close to fully solidified zone, different mechanism dominates the coarsening, apparently (Fig. 3). Secondary arms continue to occupy the narrow inter-arm spaces, driving on enriched melt in narrower or broader gaps, from one to another, finally fill up the inter-arm space together with primary bodies, eventually in cooperation with inclusions.

4.3. Solidification-Unit-Cell and Solute-Enriched-Net-work/Node

In order to depict a precise model for dendrite structure, one has to know the exact shape and dimensions of it. A tri-angular model enclosed by three dendrites arrays of hexagonal ellipsoid/paraboloid is attractive for conceptual interpretation, but lacks preciseness from quantitative point of view. Jacobi *et al.*¹⁾ observed arrays of primary arms of steady state

Fig. 9. Arrays of primary dendrite arms in steady state solidification of steels (γ -primary) after Jacobi and Schwerdtfeger.¹⁾

Fig. 10. Aggregate of steady state uni-directional dendrites.

uni-directionally solidified carbon-manganese steels which have chemical compositions close to the present steels, and concluded that the complexed arrays are categorized into two patterns. Figure 9 is the reproduced figures from their work.¹⁾

Based on their findings, compact aggregate of dendrites with secondary arms are conceived and each aggregate model is depicted for each pattern. They are illustrated in Fig. 10. Type-1 in Fig. 10 is for Pattern A in Fig. 9, and Type-2 for Pattern B. Now aggregate models are prepared, the next work is obviously how to section the interface between arms adjacent to each other. In the following discussion, Type-1 for Pattern A is treated, but the discussion is applicable for Type-2 as well.

Considering crystallographic restriction of steel, there remains only one solution to the sectioning, i.e., packing a unit part of primary dendrite knuckle with a 14-facet polyhedron illustrated in Fig. 11. Three orientations of the polyhedron axes coincide with three $\langle 100 \rangle$ directions of cubic, in which γ steel-crystal growth preferentially occurs. One series stack of the 14-facet polyhedra corresponds to one primary dendrite arm with perpendicular

Fig. 11. 14-Facet polyhedron lapping a Solidification-Unit-Cell.

Fig. 12. Consistency of space-dividing by Solidification-Unit-Cell.

Fig. 13. 3-Dimensional structure of Sulfur-Enriched-Net-work. (For Type-1 aggregate).

ular secondary arms. For the compactness of aggregates of adjacent polyhedra-stacks, following conditions must be satisfied;

(1) each parallelogram in the 14-facet polyhedron must be rhombic,

(2) each pair of parallel sides in the hexagonals in the 14-facet polyhedron must be equal length.

Provided the two conditions are satisfied, aggregates of polyhedra-stacks can be compact as shown in Fig. 12. The interface of aggregates of polyhedra-stacks is thought to be an extremity where residual melts shrinkage. Therefore it is quite a reasonable idea that the 14-facet polyhedron is a unit of steady state uni-directional dendrite. In the sense the 14-facet polyhedron is named as 'Solidification-Unit-Cell' or 'S.U.C.'. The 14-facet polyhedron has the same topological nature as that of the truncated octahedron proposed by Smith.¹⁵⁾

It is easily understood that apexes, edges and facets of the polyhedron are the locations where solute elements

are ejected from steel-dendrite bodies, and sulfide- or oxide-inclusions are preferentially allocated there in the order. From this point of view, a numerical interpretation is expected to the morphology and size of inclusions. The network consisting of apexes and edges is named as 'Solute-Enriched-Network/Solute-Enriched-Node' or 'S.E.N.'. In Fig. 13 three-dimensional structure of S.E.N. is illustrated.

4.4. S.U.C., S.E.N. and Solidification Parameter: $R^{-m}G^{-n}$

Volume of a S.U.C. is related to dendrite arm spacings as shown in Fig. 11. Since the volume of S.U.C.: V_{SUC} is one half of the lattice unit volume in Fig. 11,

$$\begin{aligned} V_{\text{SUC}} &= 1/2 \times \lambda_1^{\text{II}} \times 2\lambda_1^{\text{I}} \times \lambda_2^{\text{f}} = \lambda_1^{\text{II}} \lambda_1^{\text{I}} \lambda_2^{\text{f}} \\ &= 1.17(\lambda_1^{\text{II}})^2 \lambda_2^{\text{f}} = 0.985(\lambda_1^{\text{I}})^2 \lambda_2^{\text{f}} \sim \lambda_1^2 \lambda_2^{\text{f}} \dots\dots\dots(4) \end{aligned}$$

where the results of Jacobi *et al.*¹⁾ for Pattern A array; $\lambda_1^{\text{I}} = 1.17\lambda_1^{\text{II}}$ is applied, and the method of present measuring of λ_1 is accounted as $\lambda_1 = (\lambda_1^{\text{I}} + \lambda_1^{\text{II}})/2$. Inserting Eqs. (1) and (3) into Eq. (4), we get

$$\begin{aligned} V_{\text{SUC}} (\mu\text{m}^3) &= 2.7 \times 10^9 R^{-0.42} G^{-1.5} \\ &[R (\mu\text{m/s}), G (^\circ\text{C/mm})] \dots\dots\dots(5) \end{aligned}$$

and the lengths of sides of each rhombic in Fig. 11 are;

$$\left. \begin{aligned} Rh1 (\mu\text{m}): & \sqrt{[0.0526\lambda_1^2 + 0.0625(\lambda_2^{\text{f}})^2]} = 457R^{-0.14}G^{-0.50} \\ Rh2 (\mu\text{m}): & \sqrt{[0.286\lambda_1^2 + 0.0625(\lambda_2^{\text{f}})^2]} = 961R^{-0.14}G^{-0.50} \\ Rh3 (\mu\text{m}): & 0.582\lambda_1 = 1020R^{-0.14}G^{-0.50} \end{aligned} \right\} \dots\dots\dots(6)$$

$[R (\mu\text{m/s}), G (^\circ\text{C/mm})]$

4.5. Morphology and Size of Sulfides

Since the early work of Sims,²⁵⁾ lots of works were done about the relationship between morphology of sulfide-inclusions and activity-balance of Mn-Fe-S-O in the melt where sulfide inclusions precipitate. According to the results,¹⁶⁻²²⁾ particularly the overlooking work of Steinmetz *et al.*²¹⁾ upon influence of carbon, silicon and aluminum, the manganese-sulfide in the present steels is expected to take mainly dendritic II-type morphology, eventually accompanied with III-type, provided enough time to the solidification is given, *i.e.*, the steels solidify in quasi-equilibrium state. From the results of observation shown in Figs. 4 and 5, it is clear manganese-sulfide inclusions changed the dendritic morphology, or grew the dendritic structure, below the

solidus calculated with Turkdogan's formulae³⁾ using the chemical composition of incipient steel, and finally fixed the shape as expected one.

On the way *i.e.*, between dendrite arms of solid/liquid zone where liquid still existed at quenching, eutectic II-type manganese-sulfide was predominant with iron-sulfide inclusion which partially overlapping I-type manganese-sulfide inclusion. The overlapping of iron-sulfide on manganese-sulfide became more frequent at locations where temperature at quenching was higher than the liquidus (Fig. 4). It is very interesting that iron-sulfides could be observed at every portion in steel a (0.073 mass% S), but no iron-sulfide was found in the fully solidified zone before quenching in steel b (0.046 mass% S, Figs. 4 and 5b). The difference should naturally be ascribed to old but still practising experience of reduction of FeS by Mn-addition. De Toledo *et al.*²⁶⁾ recently discuss this theme considering enrichment of manganese and sulfur in dendritic segregation. According to their MSC (manganese-sulfur-criteria) index, each value of MSC for the present steels is 0.74 for steel a, 0.79 for b, respectively, both of which are nearly equal, but a little bit lower than 'MSC > 1 criteria' proposed for high ductility, or good surface quality in continuous cast steels containing around 0.2%-carbon. Lower limit of the present higher carbon steels might suggest a reduction in critical MSC-value depends on increase in carbon content.

Ito *et al.*,²²⁾ observed behaviors of manganese-sulfide in low carbon aluminum-killed steels (appr. 0.3%C-0.5%Si-0.8%Mn in mass%) under controlled solidification conditions and quenching temperatures, and reported that II-type manganese-sulfide inclusion grew until 1380-1350°C which, presumably, is lower than the solidus of the initial steel compositions by 100°C or more.

The present result is very similar to them, adding that there exists a difference between the temperature where the dendritic II-type manganese-sulfides finish growing (Fig. 5) and the temperature where increase in secondary dendrite arm spacing of steel saturates (Fig. 3). The former ends at lower temperature range, presumably at below 1300°C, but the latter around 1300°C. Particularly iron-sulfide inclusions increase the size and decrease the distribution density until lower temperature range than manganese-sulfide does, as shown in Fig. 5a.

These results can be explained using a ternary Fe-Mn-S-diagram (Fig. 14) in which the data of Fischer²⁴⁾ is joined with the former results.^{18,19,23)} The solidifying behavior of the residual melts in the S.E.N. illustrated in Fig. 13, appears differently depending on

Table 7. Measured values relating to dendrite structures, sulfides, $R^{-m}G^{-n}$ and V_{SUC} .

Test No.	R ($\mu\text{m/s}$)	G ($^\circ\text{C/mm}$)	Θ_f (s)	λ_1 (μm)	λ_2^{f} (μm)	d_{MnS} (μm)	d_{FeS} (μm)	$R^{-0.14}G^{-0.15}$ ($R: \mu\text{m/s}, G: ^\circ\text{C/mm}$)	V_{SUC} (μm^3)
9	28.7	1.99	1150	862	316	7.8	12.0	0.440	2.70×10^8
5	56.2	1.81	648	717	301	6.8	11.0	0.419	1.78×10^8
3	28.8	4.81	474	474	257	4.4	7.6	0.283	0.664×10^8
11	21.8	16.3	185	272	172	4.2	7.0	0.160	0.146×10^8
12	5.28	2.04	5310	910	434	9.4	—	0.552	4.13×10^8
13	4.97	4.83	2360	626	362	8.0	—	0.362	1.63×10^8
17	4.12	10.9	1270	462	228	5.6	—	0.247	0.560×10^8

Fig. 14. Interpretation on dendritic segregation and precipitations of sulfide-inclusions in residual melts in terms of Fe-Mn-S equilibrium diagram.

relative enrichment of sulfur characterized with Mn/S-rate. In higher Mn/S-rate in S.E.N., the solidifying process leans to Fe-Mn-side in Fig. 14, resulting in MnS-rich iron-manganese-sulfide, consequently with higher local solidus: T_{LS} . The temperature where solidifying of S.E.N. completes ranges from high T_{LS} shown with $\langle B' \rightarrow B'' \rightarrow Y \rangle$ root to lower one with $\langle B' \rightarrow Y' \rangle$ root depending on Mn/S-rate. On the contrary, further lower Mn/S-rate leads to iron-rich composition in S.E.N. as shown $\langle A' \rightarrow A'' \rightarrow X \rangle$, precipitating FeS-rich iron-manganese-sulfide with lower solidus. Precipitation of eutectic II-type manganese-sulfides in such melts lowers Mn/S-rate further as $\langle X \rightarrow X' \rangle$ root, finally intrigues the precipitation of iron-sulfide inclusions there as observed in Fig. 4 columns F and G. In each case, when concentrations of manganese and sulfur exceed a solubility-product of an iron-manganese-sulfide, which ordinarily is called simply 'manganese-sulfide' or 'iron-sulfide', then the inclusions begin to precipitate with corresponding morphologies explained in the followings.

The solidifying process of iron-manganese-sulfide is also controlled by local chemical composition and local solidification variables. According to Steinmetz's interpretation,²¹⁾ it is thought that morphology of a manganese-rich iron-manganese-sulfide inclusion depends on the activity of manganese: a_{Mn} in S.E.N.. If a_{Mn} in S.E.N. is high enough, morphology of the inclusion exhibits dendritic form depending on its crystallographic system. This is called dendritic, or skelton-like, manganese-sulfide. Lower a_{Mn} in S.E.N. gives eutectic, or coral, manganese-sulfide which is observed in Fig. 4, column: D-F. Both are categorized in II-type, but each has different conditions to precipitate. The eutectic manganese-sulfide inclusions in the columns of Fig. 4 must have appeared during quenching, not before quenching *i.e.*, just before quenching the area contouring the eutectic rods was, still melt, in another words, the location: F in Fig. 4 where the temperature is estimated to be T_s ($\sim 1430^\circ\text{C}$)

Fig. 15. Relationship between Solidification-Unit-Cell volume and mean diameter of MnS-dendritic rods.

contained enriched liquid and the secondary arms of steel were still active, presumably, in coalescence reaction.¹²⁾

In the steel melt which had further lower a_{Mn} through inadequate enrichment of manganese, hence appropriate reduction by manganese could not work, iron-rich phase usually denoted as FeS precipitated. This kind of sulfide inclusion was not dendritic but blocky or spherical, which should not be regarded as intrinsic morphology of FeS. It is thought three-dimensional restraint by steel-matrix circumferencing the residual melt pool in S.E.N. fix the morphology and the size, although the inclusion would have taken dendritic or eutectic rod form in free liquid melt.

Understood the above explanations about the precipitation kinetics of sulfides, diameter of dendritic iron-manganese-sulfide inclusions at the solidified portion before quenching shall be related to the local solidification variables as steel-dendrite are. Indeed the relationships between S.U.C.-volume: V_{SUC} and d_{MnS}/d_{FeS} ; calculated diameters of Mn-rich/Fe-rich iron-manganese-sulfides are satisfactorily good as shown in Fig. 15. These relations are expressed with Eqs. (7) and (9). This means the local solidification variables, or local solidification parameter, for iron-manganese-sulfide solidification has much to do with sulfide-dendrite arm spacing. From applicational view point, however, calculating the local solidification variables in the residual melt does not seem to be a useful work, because they are ruled by the solidification variables of overall system and steel dendrite arm spacings which, again, are controlled by overall solidification parameter.

Since V_{SUC} is given with Eq. (5), mean diameters of iron-manganese-sulfide rods are related to the solidification parameter of the whole system as follows;

$$d_{MnS} (\mu\text{m}) = -23.5 + 3.8 \log V_{SUC} \quad (V_{SUC}: \mu\text{m}^3) \quad \dots\dots\dots(7)$$

$$= 12.3 + 11.4 \log R^{-0.14} G^{-0.50}$$

$$(R: \mu\text{m/s}, G: ^\circ\text{C/mm}) \quad \dots\dots\dots(8)$$

Fig. 16. Relationship between solidification parameter and mean diameter of MnS-dendritic rods.

$$d_{\text{FeS}} (\mu\text{m}) = -20.6 + 3.851 \log V_{\text{SUC}} \quad (V_{\text{SUC}}: \mu\text{m}^3) \quad \dots (9)$$

$$= 15.7 + 11.6 \log R^{-0.14} G^{-0.50} \quad (R: \mu\text{m/s}, G: ^\circ\text{C/mm}) \quad \dots (10)$$

The relations of Eqs. (8) and (10) are shown in Fig. 16.

As mentioned before, the values given by Eqs. (7) and (9), or (8) and (10), are not the size of overall stretch of an iron-manganese-sulfide inclusion, but the diameter of an arm/rod of dendritic iron-manganese-sulfide as illustrated in Fig. 15. A characteristic value for a stretch might be a radius of a sphere: r_{MnS} which has the equal volume to an overall inclusion volume, which could be related to the size of S.E.N., i.e. to the dimensions of the 14-facet polyhedron (Fig. 13). Attention should be paid to the nature of dendrite morphology, where r_{MnS} is related to the S.U.C.-volume and sulfur concentration in incipient steel.

Schwerdtfeger²⁷⁾ pointed that radius of manganese-sulfide inclusions in columnar zone of 50 kg-ingot of aluminum-killed steels (appr. 0.6% C–2% Mn–0.009/0.039% S) depends on local cooling rate at solidus, but influence of sulfur content was negligibly small in the observation. The present analysis is quite consistent with the first pointing, but to the second one, more systematic experiment is needed to generalize the influence of sulfur content on the size of manganese-sulfide inclusions.

5. Conclusion

A new idea: Solidification-Unit-Cell, S.U.C., is applied to the dendrite structure/morphology formed in steady state uni-directional solidification of steel. The S.U.C. is a 14-facet polyhedron, since steel solidifies with cubic closed-pack system. Conditions for compactness of series stackings of the polyhedra are elucidated, and dimensions of the polyhedron are numerically related to solidification variables of uni-directional solidification.

Precipitation-kinetics of sulfide inclusions are interpreted with simultaneously progressing metallurgical behaviors, e.g., coarsening/coalescence of steel-dendrites, dendritic segregation of solutes. For numerical calculations of manganese-sulfide inclusions, several equations are derived based on elaborate observations of inclusions and thermodynamic considerations, taking the results above into account.

With the concept of S.U.C., and dendritic nature of II-type manganese-sulfide inclusions, it is shown that the arm thickness or arm spacings of II-type sulfides can be related to the solidification variables of the whole system, however, the size of an overall inclusion should be ruled by the volumetric size of a residual melt where the sulfides precipitate, hence again by solidification variables.

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