Effect of Sulphur on Solidification Cracking in Weld Metal of Steel (Report 2)*

-Theoretical Investigation on Change in Liquid Composition among Primary Crystals during Weld Solidification and on New Parameter Replacing Mn/S in Fe-S-Mn Alloy Steel-

By Hiroji NAKAGAWA**, Fukuhisa MATSUDA*** and Tomio SENDA**

Abstract

The effect of sulphur and manganese on the weld solidification crack in steel is usually discussed in terms of a parameter Mn|S ratio. The parameter Mn|S, however, is considered to be ambiguous in the metallurgical meaning though it is conventionally and experimentally used. On the other hand the solidification crack is closely related with the microsegregation of sulphur and manganese during the solidification. For these reasons, the change in liquid composition among cells or cellular dendrites during the weld solidification of Fe-S-Mn alloy steel is discussed using Pfann's equation in this report. Further, by analyzing the relation between the change in liquid composition theoretically deduced and the Fe-S-Mn phase diagram, a new parameter is derived. The enw parameter is shown as Mn^3/S in the case where δ phase solidifies, or Mn^5/S in the case where γ phase solidifies.

1. Introduction

It is well known that manganese is a beneficial element to prevent the detrimental effect of sulphur on the solidification crack of steel. The manganese content required is usually given as Mn/S ratio^{1,2)}. The formation limit of FeS or MnS is also given with $Mn/S^{3,4)}$. The parameter Mn/S, however, is considered to have only conventional meaning rather than a definite metallurgical meaning. Therefore a parameter with a definite metallurgical meaning should be given instead of Mn/S, though Mn/S is a useful parameter in a practical meaning for the steels which contain the same sulphur content.

On the other hand both the solidification crack and sulphide are formed at grain boundary of primary crystals (including cell or cellular dendrite boundary). Therefore, in order to obtain a new parameter, it is considered that the relation between sulphur and manganese concentrations in the remaining liquid at the intercrystalline region during the weld solidification has to be investigated.

For these reasons, in this report a theoretical equation, with which the composition of the remaining liquid during non-equilibrium weld solidification of a fundamental Fe-S-Mn alloy steel can be drawn on Fe-S-Mn phase diagram, is investigated. Further by analyzing the relation between this theoretical equation and the Fe-S-Mn phase diagram, a new parameter is deduced. This new parameter can be well applied to the sulphides and the solidification crack susceptibility in the weld metals of Fe-S-Mn alloy steels⁵.

2. Qualitative Explanation on Solidification Process of Fe-S-Mn Alloy Steel

It is necessary to clarify the solidification process of Fe-S-Mn alloy steel in order to investigate the problem above mentioned. Fe-S-Mn phase diagram⁶ and its qualitative diagram are shown in **Figs. 1(a)**



Fig. 1. Fe-S-Mn ternary equilibrium phase diagram

** H. Nakagawa is Instructor and T. Senda is Professor of Welding Department, Faculty of Engineering, Osaka University, Suita, Osaka, Japan.

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^{***} F. Matsuda is Associate Professor of Welding Research Institute of Osaka University, Suita, Osaka, Japan.

and (b) respectively. In Fig. 1(b) the curve e_1 'E is Fe-FeS eutectic curve, the curve e_2 'E is FeS-(Mn,Fe)S eutectic curve, the curve e_3 'E is Fe (containing Mn)— (Mn,Fe)S eutectic curve, and the point E is Fe-FeS-(Mn,Fe)S ternary eutectic point. In an Fe-rich Fe-S-Mn alloy steel the solidification arises in the region between the apex Fe and the curve e_1 'Ee₃', since the iron containing manganese (and also a very little amount of sulphur) solidifies as the primary phase.

The solidification process of an alloy steel whose composition is represented for example as the point A_1 or A_2 in Fig. 1(b) is as follows: The sulphur and manganese concentrations in the remaining liquid increase as the primary phase solidifies, because the distribution coefficients of both sulphur and manganese are less than unity according to Fe-S phase diagram⁷⁾ and Fe-Mn phase diagram⁸⁾. Especially the enrichment of sulphur is remarkable owing to its very small distribution coefficient. Therefore the composition of the remaining liquid gradually changes along the curve with an arrow from the point A_1 or A_2 on the phase diagram. When this curve reaches the eutectic curve $e'_{3}E$ at point b_{1} or b_{2} , (Mn,Fe)S starts to solidify. By the way, there is a point R on the eutectic curve e₃'E which shows the maximum temperature (1510°C). Because of this, the remaining liquid composition of alloy A_1 , whose curve has reached the point b_1 between the points R and E, moves toward the point E, and the solidification is finished when the remaining liquid has vanished. In some alloys which have higher sulphur contents, the remaining liquid reaches the point E, and Fe-(Mn, Fe)S-FeS ternary eutectic is formed.

On the other hand, the remaining liquid composition of alloy A_2 , whose curve has reched the point b_2 between the points R and e_3 ', moves toward the point e_3 ', and the solidification is finished when the remaining liquid has vanished.

This is the qualitative explanation on the solidification process of Fe-S-Mn alloy steel. Judging from this process, in order to obtain the new parameter it would be necessary to quantitatively describe the curve along which the remaining liquid composition changes (that is, for example, curve A_1b_1 or A_2b_2). This curve is named "changing curve in liquid composition" after this.

3. Solidification Model for Weld Solidification

Since the weld solidification is a non-equilibrium solidification, cell and/or cellular dendrite structure are formed as shown in **Photo. 1.** The "changing curve in liquid composition" must be applied to these boundaries, because sulphur and manganese segregate to these boundaries. The substructure of equiaxed crystal which is sometimes formed in the weld metal of steel can be regarded as cellular dendrite. Besides, sulphur and manganese segregate also to the grain boundary such as the columnar grain boundary. As regards the segregation this grain boundary may be approximated by the cell boundary when the cell structure is formed, or the cellular dendrite boundary



Photo. 1. Typical solidification substructure in weld metal, material: HY-130

when the cellular dendrite structure is formed.

The microsegregation to these boundaries may be approximated by the model shown in **Fig. 2.** That is, the microsegregation to the cell boundary results from the solidification process which advances perpendicular to the principal growth direction of cell



Fig. 2. Illustration of solidification process of (a) cell, (b) cellular dendrite and (c) uniaxial growth model

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and toward the boundary at L_c away from the center as shown in Fig. 2(a). Similarly the microsegregation to the cellular dendrite boundary results from the process which advances perpendicular to the growth direction of the primary or secondary arm and toward the boundary at L_p or L_s away from the center as shown in Fig. 2(b). By the way, $2L_c$ corresponds to the cell size, $2L_p$ and $2L_s$ correspond to the primary and secondary dendrite arm spacings respectively. Therefore each solidification process can be approximated as a uniaxial solidification in which the solidification length is $2L_c$, $2L_p$ or $2L_s$.

4. Theoretical Investigation on "Changing Curve in Liquid Composition"

In the uniaxial solidification which satisfies the conditions that the solute concentration in the liquid is uniform and that the solute diffusion in the solid is negligible, the solute concentration C^s in the solid at the solid-liquid interface is given by the next Pfann's equation⁹⁾ (refer to Appendix I and II in regard to the applicability of the above conditions to the weld solidification):

$$C^{s} = kC(1-g)^{(k-1)}$$
(1)

- where k: distribution coefficient of the solute at the solid-liquid interface,
 - C: initial concentration of the solute (that is, the solute content measured by chemical analysis),
 - g: fraction solidified (refer to Fig. 2(c). At the start of solidification g=0, and at the end g=1.).

The solute concentration C' in the liquid is obtained by dividing Eq. (1) by k:

$$C^{l} = C(1-g)^{(k-1)}$$
(2)

When Eq. (2) is applied to sulphur and manganese, Eqs. (3a) and (3b) are obtained:

$$C_{s}^{l} = C_{s}(1-g)^{(k_{s}-1)}$$
(3a)

- where C_s^i and C_M^i : concentrations of sulphur and manganese in the liquid respectively,
 - C_s and $C_{\mathcal{M}}$: sulphur and manganese contents, k_s and $k_{\mathcal{M}}$: distribution coefficients of sulphur and manganese.

By eliminating g from Eqs. (3a) and (3b), the relation between the concentrations of sulphur and manganese in the liquid is obtained as follows:

$$C_{S}^{l} = \frac{C_{S}}{C_{M}^{(1-k_{S})/(1-k_{M})}} C_{M}^{l} \cdots \cdots \cdots (4)$$

This Eq. (4) is the theoretical equation which gives

the change in composition of the remaining liquid during the non-equilibrium solidification on the phase diagram. That is, Eq. (4) quantitatively describes the "changing curve in liquid composition" which was already shown in Fig. 1(b).

When Eq. (4) is applied to the actual case, it becomes important that the distribution coefficients in the case where δ phase solidifies as the primary phase differ from those in the case where γ phase solidifies. In Fe-S-Mn alloy steels which contain similar contents of sulphur and manganese to those in the commercial steel, δ phase generally solidifies. The composition range of the liquid phase from which δ phase solidifies is not definite. However, it is approximately considered that the range lies between the apex Fe and the line YZ in **Fig. 3.** The point Y shows the limit composition of the liquid phase from which γ phase solidifies in Fe-S phase diagram⁷. The point Z shows the similar composition in Fe-Mn phase diagram⁸.



Fig. 3. Illustration of the composition range of liquid phase from which δ phase solidifies.

The distribution coefficient of manganese k_{M} in the case where δ phase solidifies is about 0.7 according to the liquidus and solidus lines in Fe-Mn phase diagram⁸). As regards the distribution coefficient of sulphur k_{S} it is reported¹⁰ that log $k_{S} = -1.042$ (that is, $k_{S} = 0.091$) in Fe-S binary alloy steel. When manganese coexists, however, k_{S} gradually increases up to about 0.12 together with the manganese content¹⁰. From these facts, the value 0.1 as k_{S} is adopted in this report. By substituting these values into Eq. (4), the "changing curve in liquid composition" for the case where δ phase solidifies becomes:



Fig. 4. An example of "changing curve in liquid composition". curve a: $k_S = 0.1$ and $k_M = 0.7$, curve b: $k_S = 0$ and $k_M = 0.8$

$$C_{S}^{\iota} = (C_{S}/C_{M}^{3})C_{M}^{\iota^{3}} \qquad \cdots \cdots \cdots (5)$$

By way of example Eq. (5) is illustrated as curve a in **Fig. 4** for the case in which the sulphur content $C_s = 0.05\%$ and the manganese content $C_{\mathfrak{M}} = 0.5\%$.

On the other hand both carbon and nickel which are the important elements in the steel are γ phase stabilizers. Therefore γ phase solidifies in a steel containing carbon and/or nickel over a limit content. The "changing curve in liquid composition" for such asteel may be approximated by that of Fe-S-Mn alloy steel in which γ phase solidifies as the primary phase, because of the next three reasons: (1) Carbon does not form sulphide in the steel. (2) The sulphide-forming tendency of nickel is smaller than that of iron¹¹. (3) The solid solubility of nickel in MnS is small ($<10^{0}/_{0}$)¹².

The distribution coefficient of manganese k_{M} in the case where γ phase solidifies is about 0.8 according to Fe-Mn phase diagram⁸). As regards k_{S} the value zero was adopted, because $k_{S} = 0.0004 \sim 0.004$ according to Fe-S phase diagram⁷). By substituting these values into Eq. (4), the "changing curve in liquid composition" for the case where γ phase solidifies becomes:

$$C_{s}^{\iota} = (C_{s}/C_{M}^{5})C_{M}^{\iota^{5}} \qquad \cdots \cdots \cdots (6)$$

Eq. (6) is illustrated as curve b in Fig. 4 for the case in which $C_s = 0.05\%$ and $C_{\rm M} = 0.5\%$.

5. Derivation of New Parameters Replacing Conventional Mn/S

According to Eq. (4), steels in which their compositions are not the same, but the values of $C_S/C_M^{(1-k_S)/(1-k_M)}$ (or $C_M^{(1-k_S)/(1-k_M)}/C_S$) are the same have the same "changing curve in liquid composition", though their starting points of the "changing curves in liquid composition" are different. In other words, in the steels which have the same value of $C_M^{(1-k_S)/(1-k_M)}/C_S$ the compositions of their remaining liquids undergo the same change in the process of solidification, though their initial compositions and thus their liquidus temperatures are different from each other.

Therefore the compositions of the remaining liquids reach the same point on the eutectic curve e_3 'E in Fig. 1(b). These remaining liquids after reaching the same point shift on the eutectic curve with the subsequent temperature drop, and are considered to finish their solidification at nearly the same temperature. Consequently the sulphides must have almost the same structure and shape in these steels which have the same value of $C_{\rm M}^{(1-k_S)/(1-k_M)}/C_s$. Moreover according to Eq. (4), the smaller the value of $C_{\rm M}^{(1-k_S)/(1-k_M)}/C_s$ is, the higher the sulphur concentration in liquid C_s^i at constant $C_{\rm M}^i$ becomes. That is, FeS of low melting point is easily formed in a steel which has a small value of $C_{\rm M}^{(1-k_S)/(1-k_M)}/C_s$.

Further the temperature at which the solidification is finished, namely the true solidus temperature largely varies depending on the value of $C_{\mathcal{M}}^{(1-k_S)/(1-k_{\mathcal{M}})}/C_s$, because the eutectic temperature of e_3 'E ranges between 1510°C and about 988°C as already mentioned. Meanwhile, the change in liquidus temperature due to the variation of the composition was small among the commercial steels according to the results of thermal analysis. Therefore the solidification crack susceptibility, which is closely related with the temperature range between liquidus and solidus, is considered to be dependent on the value of $C_{\rm M}^{(1-k_{\rm S})/(1-k_{\rm M})}/G_{\rm S}$.

 $C_{M}^{(1-k_{S})/(1-k_{M})}/C_{S}$ becomes C_{M}^{3}/C_{S} in the case where δ phase solidifies from Eq. (5), or Mn^{3}/S in the conventional expression. On the other hand in the case where γ phase solidifies it becomes C_{M}^{5}/C_{S} or Mn^{3}/S from Eq. (6).

From these analyses, it is considered that the structure and shape of the sulphides and the solidification crack susceptibility depend on the parameter Mn^3/S in steels where δ phase solidifies, while they depend on Mn^5/S in steels where γ phase solidifies.

6. Conclusions

The change in the liquid composition during the non-equilibrium weld solidification of Fe-S-Mn alloy steel was theoretically investigated. Further, a new parameter replacing the conventional Mn/S was theoretically deduced. Main conclusions obtained are as follows:

(1) Under the conditions that the solute concentration in the remaining liquid among the growing cells or cellular dendrites is uniform and that the solute diffusion in the solid is negligible, the sulphur concentration C_s^i and the manganese concentration $C_{\mathfrak{M}}^i$ in the remaining liquid change on Fe-S-Mn phase diagram along the "changing curve in liquid composition" which isgiven by:

$$C_{S}^{t} = \frac{C_{S}}{C_{\mu}^{(1-\boldsymbol{k}_{S})/(1-\boldsymbol{k}_{M})}} C_{M}^{t}^{(1-\boldsymbol{k}_{S})/(1-\boldsymbol{k}_{M})}$$

where C_s and $C_{\mathcal{M}}$: sulphur and manganese contents in steel respectively, k_s and $k_{\mathcal{M}}$: distribution coefficients of sulphur and manganese.

When δ phase solidifies, the above equation becomes:

$$C_{S}^{l} = (C_{S}/C_{M}^{3})C_{M}^{l^{3}}$$

When γ phase solidifies, the above equation becomes:

$$C_{s}^{l} = (C_{s}/C_{M}^{5})C_{M}^{l^{5}}$$

(2) By analyzing the relation between the "changing curve in liquid composition" and Fe-S-Mn phase diagram, it is considered that the structure and the shape of sulphides and the solidification crack susceptibility depend on a new parameter $C_{\mathcal{M}}^{(1-k_S)/(1-k_M)}/C_s$. When δ phase solidifies, this parameter becomes $C_{\mathcal{M}}^{3}/C_s$ or Mn^3/S in the conventional expression. On the other hand, when γ phase solidifies, this parameter becomes $C_{\mathcal{M}}^{5}/C_s^{5}$ or Mn^5/S .

(3) The uniform solute concentration in the remaining

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liquid and the negligible solute diffusion in the solid during the weld solidification are approximately estimated for the various welding conditions.

Appendix I On the Solute Distribution in Remaining Liquid

Eq. (1) above mentioned is valid under the conditions that the solute concentration in the remaining liquid is uniform and that the solute diffusion in the solid is negligible. Therefore the applicability of the conditions to the weld solidification must be examined.

The reason why the solute concentration in the remaining liquid does not become uniform during the non-equilibrium solidification is that both sulphur and manganese are ejected from the solid-liquid interface into the liquid. When the ejected solute cannot diffuse enough into the liquid, a diffusion layer is formed at the vicinity of the interface as shown by the broken line in **Fig. 5.** When the ejected solute can diffuse enough over the liquid, however, the solute concentration in the liquid becomes uniform as shown by the solid line in Fig. 5. The condition that the solute concentration can be considered uniform as the result of diffusion is given by^{13,14}:



Fig. 5. Qualitative explanation of solute distribution in liquid during solidification

$$D^{\prime} \cdot t/L^2 \gg 1$$
(7)

- where D': diffusion coefficient of solute in the liquid L: one half of the cell size $(2L_c)$ or the dendrite arm spacing $(2L_p \text{ or } 2L_s)$, (refer to Fig. 2),
 - t: local solidification time.

The local solidification time *t* is given by:

$$t = \Delta T/R_c$$
(8)

- where ΔT : temperature range between liquidus and solidus, that is, solidification temperature range, R_c : cooling rate.
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 ΔT of the commercial steel can be estimated at 50~100°C, judging from some reports^{15,16}).

As regards L in Eq. (7), the cell size $(2L_c)$ and the primary dendrite arm spacing $(2L_p)$ are generally nearly equal, and the secondary dendrite arm spacing $(2L_s)$ is smaller than them. Moreover the cellular dendrite is more commonly formed than the cell in the weld metal. Therefore it is enough to adopt L_p as L for the examination of Eq. (7). **Fig. 6** shows the



Fig. 6. Relation between cooling rate R_c and primary dendrite arm spacing $2L_p$

relation between the cooling rate R_c and the primary dendrite arm spacing $2L_p$. The experimental points are obtained from an ingot solidification¹⁴), and the shadowed portion is obtained from a weld solidification¹⁷). According to Fig. 6, the relation between log R_c and log $2L_p$ can be represented by a straight line. This relation is approximately given by:

$$=1.6 \times 10^{-2} R_c^{-0.44} \text{ (cm)} \cdots (9')$$

Therefore

By substituting Eqs. (8) and (9") for Eq. (7), 5×10^{-5} cm²/sec¹⁸⁾ for D^{I} , and $50 \sim 100^{\circ}$ C for ΔT , the left side of Eq. (7) becomes:

$$D^{I} \cdot t/L_{p}^{2} = (3.9 \sim 7.8) \times 10 R_{c}^{-0.12} \cdots (10)$$

Eq. (10) is illustrated in **Fig. 7.** According to Fig. 7, $D^{t} \cdot t/L_{p}^{2}$, which decreases gradually with the cooling rate, is above about 20 even at the cooling rate of 1000°C/sec which is a considerably large cooling rate in the weld solidification. From this result it is considered that the relation of Eq. (7) is almost valid for various welding conditions.



Fig. 7. Relation between cooling rate R_c and $D't/L_p^2$

Appendix II On the Solute Diffusion in Solid

The condition that the solute diffusion in the solid is negligible during the solidification is given by¹⁹:

where k: distribution coefficient,

 D^s : diffusion coefficient of solute in the solid.

The diffusion coefficients of sulphur and manganese

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at $1400 \sim 1500^{\circ}$ C are shown in **Table 1**. These diffusion coefficients are extrapolated from the experimental results²⁰⁾ in γ phase, because those in δ phase have not been measured.

Table 1. Diffusion coefficients D^s of sulphur and manganese in solid iron at 1400..1500°C

Element	$D^s (\mathrm{cm}^2/\mathrm{sec})$
S	$(4.7\sim 8.7) \times 10^{-8} (D_0 = 2.46 \times 10^{-3} \text{ cm}^2/\text{sec}, Q = 36.1 \text{ kcal/mole}^{20})$
Mn	$(9.0 \sim 25) \times 10^{-10} \ (D_0 = 5.5 \times 10^{-2} \ \mathrm{cm}^2/\mathrm{sec}, Q = 59.6 \ \mathrm{kcal/mole}^{20})$

For the examination of Eq. (11) it is enough to adopt L_s as L which has the smallest value among L_c , L_p and L_s as already mentioned. Fig. 8 shows the relation between the cooling rate R_c and the secondary dendrite arm spacing $2L_s$. The experimental points are obtained from the ingot solidification¹⁴, and the shadowed portion is obtained from the weld solidification¹⁷). According to Fig. 8 the relation between $\log R_c$ and $\log 2L_s$ can be represented by a straight line, and this is approximately given by:



Relation between cooling rate R_c and secondary Fig. 8. dendrite arm spacing $2L_s$

 $2L_s = 70R_c^{-0.46} (\mu)$ $\cdots \cdots \cdots (12)$

$$=7.0 \times 10^{-3} R_c^{-0.46} (\text{cm}) \cdots (12')$$

Therefore

By way of example the case where δ phase solidifies is shown. By substituting Eqs. (8) and (12'') for Eq. (11), and 0.1 for the distribution coefficient of sulphur, 0.7 for that of manganese, and the value in Table 1 for D^s , the left side of Eq. (11) becomes:

$$kD^{s}t/L_{s}^{2} = (1.9 \sim 7.1) \times 10^{-1}R_{c}^{-0.08}$$

for sulphur(13)

$$kD^{s}t/L_{s}^{2} = (0.26 \sim 1.4) \times 10^{-2}R_{c}^{-0.08}$$

for manganese(14)

Eqs. (13) and (14) are illustrated in Fig. 9. According to Fig. 9 the solute diffusion in the solid is considered to be approximately negligible in various welding conditions. Especially for sulphur, the solute diffusion in the solid is further negligible in the case where γ phase solidifies, because the distribution coefficient becomes approximately zero as already mentioned.



Fig. 9. Relation between cooling rate R_c and kD^st/L_s^2

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