Influence of Sulphur Content and Molten Steel Flow on Entrapment of Bubbles to Solid/Liquid Interface

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The sliver defects which occur easily on ultra low carbon steel sheet are the most harmful defects, especially to automobile outer panel products. There may be many causes of the sliver defects such as nonmetallic inclusions, bubbles, surface cracks and inner cracks. However, crack formation is not a serious problem in continuously cast ultra low carbon steel because of its good ductility at high temperatures. Therefore, it is important to reduce the amount of nonmetallic inclusions and bubbles just below the slab surface. Electro-Magnetic Stirring in the mold (M-EMS) is an effective tool to remove such bubbles and reduce the amount of the sliver defects, although the effects of M-EMS on the reduction in sliver defects are influenced by the chemical composition of steel, especially by the sulphur content. The slabs cast at No.4CC-1 strand in Kakogawa Works reveal rather a high content of bubbles when the sulphur content is higher and M-EMS is not applied. In this study, the reason why sliver defects caused by bubbles are more likely to occur on steel of higher sulphur content is discussed based on the interaction between advanced solid/liquid interface and bubbles. The forces acting on the bubbles are theoretically described as a function of bubble radius, velocity and interfacial tension gradient of liquid steel in front of a solid/liquid interface.

KEY WORDS: sliver defect; nonmetallic inclusion; bubble; M-EMS; sulphur content; solid/liquid interface; interfacial tension gradient; radius.

1. Introduction

In order to improve the surface quality of the production of ultra low carbon steel sheet used for automobiles, it is important to reduce the nonmetallic inclusions and bubbles (blowhole defects) which exist just below the surface of continuously cast slab. Al₂O₃ clusters are often found on the inner surface of a bubble¹ as shown in Fig. 1.

Therefore, reducing the bubbles is helpful for preventing the accumulation of nonmetallic inclusions below the surface. It is well known that the distribution of bubbles depends on the steel grade, especially on the sulphur content. Figure 2 shows the relationship between sulphur content in steel and the number of sliver defect of ultra low carbon steel at KAKOGAWA Works. Figure 3 shows the morphology of various kind of sliver defects at the cast stage. The vertical axis shows the estimated length of sliver defects in slab which is calculated from the length of sliver in coil considering with reduction ratio. The original shape of sliver is approximately spherical, except Al₂O₃ clusters and wide defects presumably caused by the scarfer. The main shapes of slivers at KAKOGAWA Works are classified in TYPE B and TYPE C shown in Fig. 3. From Figs. 1–3, bubbles are assumed to be the main cause of sliver defects and the number of bubbles are strongly affected by sulphur content in molten steel. Several authors reported that this
phenomenon can be explained by the force acting on the bubble which is caused by the interfacial tension gradient between bubble and solute boundary layer which exists at the solidification front.2,3) However, there are few studies which examine the behavior of “bubbles of millimeter scale” that become an actual product defect. In this study, the effects of the sulphur content of steel and the flow velocity of M-EMS on the capturing effect of “bubbles of millimeter scale” to the solidified shell was investigated quantitatively.

2. Experimental

Continuously cast slabs of ultra low carbon steel whose chemical compositions are shown in Table 1 were cast in 2 heats/sequence at No.4CC-1str in Kakogawa Works at Kobe Steel, Ltd. The casting conditions are shown in Table 2. Only the sulphur content has been changed in each heat to evaluate its influence. Moreover, two kinds of slab samples were taken from the stable period of each heat, one with M-EMS and the other without M-EMS. The samples were processed to 160 test pieces (80 pieces/wide face×2) as shown in Fig. 4. A cross section of each sample was etched by picric acid solution and the solidification structure was identified. Thus, the ‘Nail-like’ structure at just below an oscillation mark (OSM) was observed. Then, an X-ray penetrating test was carried out for each 10 mm thick sliced sample that was taken from whole wide of slab and all blowholes over 0.3 mm in diameter trapped within 20 mm regions from the surface were counted. The depth of blowhole defects from the slab surface was also measured.

3. Results

3.1. Results of Investigation of ‘Nail-like’ Structure at Oscillation Marks

Examples of the solidification structure at the OSM portion and blowhole defects are shown in Fig. 5. In the subsurface region, blowholes are observed and ‘Nail-like’ structures are often seen on them. Figure 6 shows the effects of M-EMS on the depth of ‘Nail-like’ structures and its occurrence ratio. The depth of ‘Nail-like’ structures be-
comes shallow and the incidence of ‘Nail-like’ structures at the OSM portion also decreases when M-EMS is applied.

3.2. Distribution of Blowholes
The distribution of blowhole defects over 0.3 mm in diameter in the region of 20 mm from the slab surface is shown in Fig. 7. By applying M-EMS, the number of blowholes decreases, especially in the subsurface (~10 mm) region.

3.3. Size Distribution of Blowholes
The size distribution of blowholes is shown in Fig. 8. When using M-EMS, the number of blowholes decreases regardless of size or sulphur content. Moreover, the number of blowholes also decreases when the sulphur content is lower.

3.4. Removal Efficiency of Bubbles by M-EMS
For each size of blowhole, the removal efficiency (R.E.) by M-EMS is defined by Eq. (1).

\[ R.E. = \frac{N_{\text{without M-EMS}} - N_{\text{with M-EMS}}}{N_{\text{without M-EMS}}} \] (1)

where, \( N \) is the number of blowholes.

It can be noticed that R.E. becomes large when the level of sulphur content is low as shown in Fig. 9. Sulphur content does not affect R.E. for the blowholes whose diameter is over 1.1 mm.

4. Discussion
Molten steel flow parallel to the liquid/solid interface caused by M-EMS washes bubbles away from the interface of the solidified shell, and it decreases the number of blowholes in the subsurface of a slab. Moreover, it can be recognized that the decrease in the number of blowholes is prominent when the sulphur content is low.

4.1. Effect of Sulphur Content on the Non-uniformity of Sub-surface Solidification Structure
Non-uniformity of solidification structure is considered to be trapping sites for bubbles in the subsurface. To estimate the non-uniformity of solidification structure in the subsurface, the average depth of ‘Nail-like’ structure below each OSM was measured in case of high sulphur content steel and low sulphur content steel, respectively. The average depth of ‘Nail-like’ structure was defined as follows and shown in Fig. 10.
(average depth of ‘Nail-like’ structure)  
= (depth of ‘Nail-like’ structure) × (occurrence ratio of ‘Nail-like’ structure at OSM portion)

In case that sulphur content is high, the average depth of ‘Nail-like’ structure becomes shallow as shown in Fig. 10. However, high sulphur content steel captures more bubbles than low sulphur content steel as shown in Fig. 7 or Fig. 8. Moreover, shown in Fig. 9, low sulphur content steel has good removal efficiency by M-EMS despite it has more non-uniform structure than high sulphur content steel. Therefore, the increase of blowhole defects cannot only be attributed to an increase of the non-uniformity of solidification structures.

4.2. Force Acting on Bubbles Existing in Front of Solid/Liquid Interface

The gradient of solute concentration caused by micro segregation formed in front of the advancing solid/liquid interface results in an interfacial tension gradient in this area. Mukai et al. indicated bubbles existing in this boundary layer are forced toward the solid/liquid interface due to the interfacial tension gradient. On the contrary, bubbles existing in the velocity boundary layer induced by M-EMS are subjected to a lifting force (Saffman force) apart from the solid/liquid interface. Therefore, to examine the balance of these forces, the calculation is carried out based on the method that had been proposed by Mukai et al. Equations (2)–(7) were used to calculate the behavior of bubbles, and further, the following newly adopted concepts are taken into consideration.

1. A bubble whose diameter is much larger than the thickness of the concentration boundary layer was considered.
2. The molten steel flow velocity was taken into account to determine the thickness of the solute boundary layer.

\[
F_y(x') = -\frac{2\pi}{r} \int_{x'}^{x} \sigma'(X) \left(r^2 - (X - x')^2\right) dX \quad \ldots(2)
\]

\[
F_y(X) = 6.48 \mu \times u_y \times \frac{\partial u_y}{\partial X} \times \frac{r^2}{\sqrt{\nu}} \quad \ldots(3)
\]

\[
\sigma'(X) = \frac{d\sigma}{dX} = \frac{d\sigma}{dC_L} \times \frac{DC_L}{dX} \quad \ldots(4)
\]

\[
C_L = C_0 \times \left(1 - K_0 + (1 - K_0) \times \exp(-V_s x - \delta_c/D_L)\right) \quad \ldots(5)
\]

\[
K_0 = K_0' \times \left(1 - K_0 + (1 - K_0) \times \exp(-V_s x - \delta_c/D_L)\right) \quad \ldots(6)
\]

\[
\sigma = 1.970 - 0.170 \ln(1 + 840C_0) \quad \ldots(7)
\]

where, \(r\): radius of bubble (m), \(\sigma\): interfacial tension gradient between bubble and molten steel, in other words, surface tension gradient of molten steel (N/m), \(\mu\): viscosity (N·s/m²), \(\nu\): kinetic viscosity (m²/s), \(u_y\): the velocity component of molten steel parallel to solid/liquid interface (m/s), \(C_L\): sulphur content in solute boundary layer (mass%), \(C_0\): sulphur content in bulk (mass%), \(x'\): distance from solid/liquid interface to bubble (m), \(K_0\): equilibrium distribution coefficient (—), \(V_s\): velocity of molten steel at liquid/solid interface (m/s), \(\delta_c\): solute boundary layer thickness (m), \(D_L\): diffusion coefficient of sulphur in liquid (m²/s).

The parameters used in the calculations are listed in Table 3, where \(\delta_c\) is calculated from Eqs. (8)–(11) as follows.

\[
\text{Sh} = 0.662 \text{Re}^{1/2} \text{Sc}^{1/3} \quad \ldots(8)
\]

\[
\text{Sh} = L/\delta_c \quad \ldots(9)
\]

\[
\text{Re} = u_y L / \nu \quad \ldots(10)
\]

\[
\text{Sc} = \nu / D_L \quad \ldots(11)
\]

where, Sh: Sherwood number, Re: Reynolds number, Sc: Schmidt number, L: half stroke of non-uniformity of first solidified shell, \(u_y\): velocity of molten steel flow.

The velocity distribution of molten steel, \(u_y\), was calculated by using \(k-\varepsilon\) model as a turbulence model. This simulation has been carried out by using the commercial fluid flow analysis code FLUENT. The propriety of the numerical results obtained by FLUENT have been confirmed by our previous investigations of the deflection angle of dendrites in low carbon and middle carbon steel. When using M-EMS, the molten steel flow velocity at 10 mm apart from solid/liquid interface and parallel to the solid/liquid interface becomes 0.4 m/s, and \(\delta_c\) is 10.7 \(\mu\)m at that time. Without M-EMS, the molten steel flow velocity 10 mm apart from solid/liquid interface and parallel to the solid/liquid interface becomes 0.1 m/s, and \(\delta_c\) is 21.5 \(\mu\)m. \(\delta_c\) is chosen from the values calculated by Toh et al. \(\delta_c\) becomes 1000 \(\mu\)m with M-EMS and 3000 \(\mu\)m without M-EMS. The forces acting on a bubble are schematically shown in Fig. 11.

The forces induced by the interfacial tension gradient, \(F_y\), and buoyancy, \(F_B\), were calculated and \(F_y/F_B\) is shown in Fig. 12, as functions of molten steel flow velocity and the diameter of a bubble. In this case, it is supposed that a bubble

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Table 3. Parameter values for calculation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Diameter of bubble, (2r)</td>
<td>2–1,000 (\mu)m</td>
</tr>
<tr>
<td>Thickness of concentration boundary layer, (\delta_c)</td>
<td>10.7 (\mu)m with M-EMS, 21.5 (\mu)m without M-EMS</td>
</tr>
<tr>
<td>Thickness of velocity boundary layer, (\delta_c)</td>
<td>1,000 (\mu)m with M-EMS, 3,000 (\mu)m without M-EMS</td>
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ble is in contact with the solid/liquid interface. When the ratio of the \( F_c \) to \( F_f \) increases the bubble is easier to move towards the solidified shell. If the diameter of bubble is less than 50 \( \mu \text{m} \), \( F_c \) reaches up to 5 000–50 000 times as large as \( F_f \).

Figures 13 and 14 show the relationship between the location of a bubble and \( F_c \), as the functions sulphur content and molten steel flow velocity (in case with and without M-EMS). Figure 13 is the case of a bubble of 10 \( \mu \text{m} \) in diameter and Figure 14 is of 1 000 \( \mu \text{m} \) in diameter. In both cases, higher sulphur content and lower molten steel flow rate (not applying M-EMS) leads to higher \( F_c \). It is also recognized that in the case that a bubble exists more than 20 \( \mu \text{m} \) away from solid/liquid interface, \( F_c \) becomes very small. Figure 15 shows the relationship between the diameter of a bubble and the force induced by the interfacial tension gradient and the Saffman force caused by the velocity gradient. The results are shown in the case that a bubble is in contact with the solid/liquid interface. The solid line is for the case with M-EMS and dotted line without M-EMS.

If a bubble exists 10 \( \mu \text{m} \) apart from the solid/liquid interface, the force acted on the bubble is shown in Fig. 16. It was cleared that \( F_c \) decreases drastically when a bubble is apart from the solid/liquid interface. The thickness of the solute boundary layer is 10.7 \( \mu \text{m} \) with M-EMS and 21.5 \( \mu \text{m} \) without M-EMS. Therefore, a bubble is affected very much only when the diameter of the bubble is as small as the thickness of the solute boundary layer or the bubble is soaked fully in the solute boundary layer. On the other hand, the thickness of the molten steel flow velocity boundary layer is 1 000 \( \mu \text{m} \) or 3 000 \( \mu \text{m} \) whether M-EMS is used or not. Therefore, when dealing with a bubble up to 1 000 \( \mu \text{m} \) in diameter, it is soaked in the velocity boundary layer fully and \( F_u \) grows according to the diameter.

If \( F_u + F_c > 0 \), then a bubble may go away from the
The value of $F_u/H_{11001}$ changes with the diameter of a bubble and the sulphur content. The critical bubble diameters, whether captured by the solid/liquid interface or not, were calculated and are shown in Fig. 17, under the casting conditions shown in Table 2 beforehand and a bubble is in contact with the solid/liquid interface.

The solid arrows show the effects of the increase in molten flow velocity due to M-EMS and the dotted arrows mean the effects of the decrease in sulphur content. Figure 17 shows that a bubble under 1000 mm in diameter can be removed easily when using M-EMS or by decreasing sulphur content, and a bubble over 1000 mm in diameter can be easily removed under normal casting conditions regardless of sulphur content. This agrees with the results of the distribution of bubble behavior shown in Fig. 9.

Figure 18 shows the influence of M-EMS on the diameter of bubbles. $\Delta F_u$ (or $\Delta F_c$) is defined as an absolute value of the difference between $F_u$ (or $F_c$) with M-EMS and without M-EMS. $\Delta F_u/\Delta F_c$ becomes over 1 when the diameter of a bubble is smaller than 400 mm. This means that the reason for the removal of a smaller bubble (less than 400 mm in diameter) is mainly the decrease of $F_c$. On the other hand, a bigger bubble (more than 400 mm in diameter) can be eliminated mainly by the increase of $F_u$.

5. Conclusions

The distribution of blowholes existing in the sub-surface of slabs cast at No.4CC-1 str in Kakogawa Works was investigated and the effects of the sulphur content and the velocity of molten steel flow on the distribution of blowholes were discussed.

(1) The number of blowholes less than 400 mm in diameter decreases as the sulphur content is lowered. This is attributed to the fact that the force induced by the interfacial tension gradient decreases, and the application of M-EMS also decreases this force. This is because of the decrease in the interfacial tension gradient force which is due to a decrease in the thickness of concentration boundary layer.

(2) Blowholes over 1 mm are easily removed from the solid/liquid interface by the Saffman force induced by molten steel flow regardless of sulphur content. In other words, bubbles up to about 1 mm$^3$ may be influenced by the interfacial tension gradient force formed by a concentration boundary whose thickness is only 20 mm or so.

(3) Due to the application of M-EMS or higher sulphur content, the average depth of ‘Nail-like’ structure becomes shallow. However, it can be recognized that there exist no relationship between the the depth of ‘Nail-like’ structure in the sub-surface of slab and the number of blowhole defects.

REFERENCES