Interfacial Properties of Molten Low Carbon Steel Containing Ti, Nb or B in Relation to the Behavior of Fine Particles in Continuous Casting Process

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(Received on April 26, 2006; accepted on July 10, 2006)

The surface tension of molten low-carbon (LC) steel containing Ti, Nb or B and the contact angle between the molten steel and solid alumina were measured using the sessile droplet method under an Ar gas atmosphere at 1 500°C, 1 575°C and 1 600°C. The results show that Ti decreases the surface tension of molten LC steel and the contact angle. The interfacial tension between molten LC steel containing Ti and solid alumina decreases with the increase in Ti content. The work of adhesion between molten LC steel and solid alumina decreases slightly at 1 550°C, but increases at 1 600°C with increasing Ti content. The addition of a small amount of Nb or B to molten LC steel decreases slightly the surface tension of the molten steel. The effect of Nb on the contact angle between molten LC steel and solid alumina is less, but B markedly decreases the contact angle when the B content increases from 0.0504 to 0.0999 mass%. It can be deduced that fine bubbles are more easily entrapped by the solidifying shell for LC steel with Ti or B than that with Nb, while fine alumina inclusions are more easily entrapped by the solidifying shell for LC steel with B than that with Ti or Nb.

KEY WORDS: surface tension; contact angle; low-carbon steel; titanium; niobium; boron; alumina; bubble.

1. Introduction

It is important to understand the behavior of fine particles, such as argon gas bubbles or non-metallic inclusions, in front of the solidifying shell in order to improve the surface quality of steel products in the steelmaking industry. As for low-carbon (LC) steel especially for automobile use, argon gas bubbles and non-metallic inclusions, which are entrapped by the solidifying shell in the continuous casting process, cause surface defects such as blow holes or slivers in steel products. Therefore, various countermeasures have been adopted to prevent these problems.1)

Concerning on the entrapment of fine particles by the solidifying interface, Mukai and Lin2–5) reported that the interfacial tension gradient, which is formed inversely by the solute concentration gradient in front of the solidifying shell, plays a significant role, based on a series of fundamental research on the motion of fine particles under the interfacial tension gradient. Moreover, Mukai and Zeze4,5) proposed a new index, Mukai-value $M$, to predict the degree of entrapment force only by the solute contents of the steel by developing their idea and reported that this index can successfully represent the effect of solute elements, especially surface active elements such as O, S or N, on the entrapment of bubbles and inclusions by the solidifying shell. However, the effect of Ti, Nb or B on the interfacial properties of LC steel has not been sufficiently researched, while these elements are commonly added to improve the deformability of steel products. In this research, the surface tension of molten LC steel containing different Ti, Nb or B contents and its contact angle with solid alumina were measured using the sessile drop method, and the behavior of bubbles and inclusions in front of solidifying shell is discussed.

2. Experimental

2.1. Apparatus

The sessile droplet method was applied in this research. Figure 1 presents a schematic diagram of the apparatus. The experimental temperature range was from 1 550 to 1 600°C. The measurement was conducted in an Ar atmosphere whose composition was Ar>99.999% and O$_2$<0.2 ppm. The argon gas at 100 ml/min was passed through an Ar purifier first and further deoxidized with magnesium chips in a magnesium furnace. The oxygen partial pressure, measured in the experiments, of the outlet gas was between $10^{-18}$ MPa and $10^{-23}$ MPa. Photographs of the droplet shape were taken with a camera, which was connected by a bellows.
2.2. Materials

Steel samples were prepared with electrolytic iron and Ti, Nb or B alloy. First, the electrolytic iron was melted in a high frequency induction vacuum furnace under Ar gas atmosphere. Carbon was added into the molten metal and the furnace was evacuated to decrease the oxygen content in the metal. Then Ti, Nb or B alloy was added into the melt to adjust the composition of the molten metal. Then the melt was cast in a mold. The cast metal was cut and polished into the required samples. The chemical composition of the samples with different Ti, Nb or B is shown in Table 1, respectively.

2.3. Procedure

A steel sample with 8 mm in diameter and 8 mm in height was polished with sandpaper to remove any surface oxide. Alumina substrate, which contained 99.8 mass% Al₂O₃ and was 25.7×25.7×2.5 mm in size, was placed on one end of an alumina support and its horizon was adjusted with two water levels. Then, the steel sample was set at the center position of the substrate surface. In order to obtain the results in a state of equilibrium, the first photograph of a steel droplet was taken at 30 min after the furnace reached the experimental temperature. Then the photographs of the metal droplet were taken every 5 min. A total of 10 to 13 photographs were taken at one experimental temperature. After an experiment, the geometric shape, surface color and position of a steel droplet were examined and its oxygen, nitrogen and aluminum contents were analyzed. The droplet contour was input into a computer with a digitizer. The surface tension of the molten LC steel was calculated by determining the contour curve with the best fit between the numerical solution to the classical Laplace equation and the experimentally measured points, according to Rotenberg’s method with software. The density, used in the surface tension calculation, of the molten LC steel containing Ti, Nb or B was measured using a modified sessile drop method. The maximum measurement errors were ±2% for surface tension and ±0.5% for contact angle in the process of calculation.

3. Results and Discussion

3.1. Surface Tension of Molten LC Steel Containing Ti, Nb or B

The surface tension of molten LC steel with different Ti was measured at 1550°C, 1575°C and 1600°C, respectively, under an argon atmosphere using the sessile drop method. The results are presented in Fig. 2 and those obtained by other researchers for Fe–Ti system are also given in Fig. 2 as a comparison with the present measurement.
It can be seen from Fig. 2 that the surface tension of molten LC steel containing Ti decreases remarkably with increasing Ti content in the present work. At low experimental temperature, the surface tension decreases more than that at high experimental temperature with the increase in Ti content. To be more precise, it can be seen that the positive temperature coefficients of surface tension are apparent for molten LC steel containing Ti, and the present measurement shows the tendency to the surface adsorption of Ti. As can be seen from Fig. 2, the influence of Ti on the surface tension of molten LC steel in the present research is similar to the results obtained by Kishimoto et al.\textsuperscript{8)} and the results of Yokoyama et al.\textsuperscript{9)} at low Ti content, that is, the addition of Ti decreases the surface tension of molten iron, but different from those obtained by Smirnov et al.\textsuperscript{10)} and Ohara et al.\textsuperscript{11)} who found that the addition of Ti does not markedly change the surface tension of molten iron.

From the following interaction parameters\textsuperscript{12)}: $e_{Ti}^{M} = -0.043, e_{Ti}^{O} = -3.4, e_{Ti}^{N} = -2.06, e_{Ti}^{P} = -0.06, e_{Ti}^{Si} = -0.27$, the Ti activity coefficient and activity in the molten LC steel can be calculated. Variation in the surface tension of molten LC steel with natural logarithm of Ti activity is presented in Fig. 3. According to the Gibbs adsorption isotherm and the Langmuir isotherm, the influence of Ti activity on the surface tension of molten LC steel can be calculated. The surface tension of molten LC steel containing Ti decreases remarkably with increasing Ti content from 0.145 to 0.200 mass% Ti in LC steel up to about 0.2 mass% [Nb] or 0.1 mass% [B] does not greatly change the surface tension of molten LC steel. Therefore, Nb and B are not as strongly surface-active as Ti in molten LC steel. The effect of boron on the surface tension of molten LC steel is similar to that obtained by Kozakevitch and Urbain,\textsuperscript{13)} Tavadze et al.\textsuperscript{14)} and Pirogov et al.\textsuperscript{15)} who also found that the addition of a small amount of B to iron does not markedly affect the surface tension. Although the surface tension of molten LC steel with Nb content of 0.198 mass% is substantially lower than that of 0.102 mass% [Nb], it should be noted from Table 1 that the sample with 0.198 mass% [Nb] has a higher O content by 0.0026 mass% than that with 0.102 mass% [Nb]. This amount of O content is considered for the decrease in surface tension from the experimental data on the surface tension of Fe–O alloys [Appendix]. Thus, the surface tension of molten LC steel with 0.198 mass% [Nb] is corrected from the solid points up to the hollow points as shown in Fig. 4.

\[ \sigma_{tg} = \sigma_{tg}^{0} - RT \ln(1 + K_{ti} a_{ti}) \]  

where $\sigma_{tg}$ and $\sigma_{tg}^{0}$ are the surface tension of molten LC steel containing Ti and molten LC steel respectively, $K_{ti}$ is the saturated surface excess concentration of Ti at the Gibbs dividing surface of $\Gamma_{LCsteel} = 0$, $K_{ti}$ is the adsorption coefficient of Ti and $a_{ti}$ is the activity of Ti in molten LC steel. By fitting Eq. (1) to the experimental data in Fig. 3, the values of $\sigma_{tg}$ were drawn with the following equations ($\sigma_{tg} / \text{mN} \cdot \text{m}^{-1}$):

\[ \sigma_{tg} = 1935 - 134 \ln(1 + 46a_{ti}) \] at 1550°C .......(2)

\[ \sigma_{tg} = 1915 - 122 \ln(1 + 24a_{ti}) \] at 1575°C .......(3)

\[ \sigma_{tg} = 1904 - 84 \ln(1 + 10a_{ti}) \] at 1600°C .......(4)

The Influence of Nb or B on the surface tension of molten LC steel is shown in Figs. 4 and 5, respectively. As can be seen from these two figures, the addition of Nb or B in LC steel up to about 0.2 mass% [Nb] or 0.1 mass% [B] does not greatly change the surface tension of molten LC steel. Therefore, Nb and B are not as strongly surface-active as Ti in molten LC steel. The effect of boron on the surface tension of molten LC steel is similar to that obtained by Kozakevitch and Urbain,\textsuperscript{13)} Tavadze et al.\textsuperscript{14)} and Pirogov et al.\textsuperscript{15)} who also found that the addition of a small amount of B to iron does not markedly affect the surface tension. Although the surface tension of molten LC steel with Nb content of 0.198 mass% is substantially lower than that of 0.102 mass% [Nb], it should be noted from Table 1 that the sample with 0.198 mass% [Nb] has a higher O content by 0.0026 mass% than that with 0.102 mass% [Nb]. This amount of O content is considered for the decrease in surface tension from the experimental data on the surface tension of Fe–O alloys [Appendix]. Thus, the surface tension of molten LC steel with 0.198 mass% [Nb] is corrected from the solid points up to the hollow points as shown in Fig. 4.

3.2. Contact Angle of Molten LC Steel Containing Ti, Nb or B on Solid Alumina

The contact angle, measured in present work, of molten LC steel containing Ti on solid alumina is given in Fig. 6. It can be found from this figure that the contact angle of molten LC steel containing Ti on solid alumina decreases slightly with a Ti concentration at 1550°C, obviously decreases with the increase in Ti content from 0.145 to 0.384 mass% at 1575°C and from 0 to 0.384 mass% at 1600°C. The contact angle of Fe–Ti alloy obtained by Kishimoto et al.\textsuperscript{8)} is also shown in Fig. 6. Their results indicate that the contact angle decreases greatly at low Ti con-
concentration ([Ti] < 0.27 mass%) and then it hardly changes with the increasing Ti content in the temperature range from 1550 to 1650°C. The contact angles obtained by them are much lower than those in the present work. Figure 7 shows the effect of Nb and B content on the contact angle of molten LC steel on solid alumina. It can be seen that the contact angle decreases slightly with the increase in Nb content. When B increases up to 0.0504 mass%, the contact angle of molten LC steel on solid alumina hardly changes, but when boron content increases further, the contact angle decreases greatly.

3.3. Interfacial Tension between Molten LC Steel Containing Ti, Nb or B and Solid Alumina

The interfacial tension between molten LC steel containing Ti, Nb or B and alumina can be calculated by the following Young’s equation,

\[ \sigma_{sl} = \sigma_{sg} - \sigma_{lg} \cos \theta \] ..................(5)

where \( \sigma_{sl} \) is the interfacial tension between molten LC steel containing Ti, Nb or B and solid alumina, \( \sigma_{sg} \) is the surface tension of solid pure alumina, \( \sigma_{lg} \) is the surface tension of molten LC steel containing Ti, Nb or B and \( \theta \) is the contact angle of molten LC steel containing Ti, Nb or B on solid alumina. Poirier et al. \(^\text{(16)}\) recommended the following formula to calculate the surface tension of solid alumina as a function of temperature from the data obtained by Overbury et al. \(^\text{(17)}\) and Cramb et al. \(^\text{(18)}\):

\[ \sigma_{sg} = 1128 - 0.1T \] ..........................(6)

where \( \sigma_{sg} \) is the surface tension of solid alumina in mN·m\(^{-1}\) and \( T \) is temperature in K. Inputting Eq. (6) and the experimental data in this work into Eq. (5), the interfacial tension of molten LC steel containing Ti, Nb or B with solid alumina can be calculated, and the results are shown in Figs. 8 and 9.

It is indicated in Fig. 8 that the interfacial tension between molten LC steel containing Ti and solid alumina decreases with the increase in Ti content. The interfacial tension at high temperature is lower than that at low temperature, but in a high Ti concentration range, the difference between interfacial tensions at different temperatures becomes small. With the same treatment method as Eqs. (2)–(4) in Fig. 3, the behavior of Ti activity on the interfacial tension of molten LC steel containing Ti with solid alumina can be described with the following equations (\( \sigma_{sl}/\text{mN·m}^{-1} \)):

\[ \sigma_{sl} = 2.585 - 117 \ln(1 + 44a_{Ti}) \] at 1550°C ............(7)

\[ \sigma_{sl} = 2.530 - 194 \ln(1 + 13a_{Ti}) \] at 1575°C ............(8)

\[ \sigma_{sl} = 2.460 - 223 \ln(1 + 8a_{Ti}) \] at 1600°C ............(9)

Figure 9 presents the influence of Nb or B on the interfacial tension between molten LC steel and solid alumina. It can
be found that the interfacial tension decreases slightly with the increase in Nb content. It should be noted that the three points at a Nb content equal to 0.198 mass% for the LC steel with Nb includes the effect of oxygen content in the sample on the surface tension \( \sigma_{bg} \) and contact angle \( \theta \). Therefore, the interfacial tension at this content should be higher. Even though B does not have a great influence on the surface tension of molten LC steel, it remarkably decreases the interfacial tension between molten LC steel and solid alumina after B content is larger than about 0.05 mass% due to its decreasing the contact angle between molten LC steel and solid alumina.

3.4. Work of Adhesion between Molten LC Steel Containing Ti, Nb or B and Solid Alumina

Work of adhesion is defined as the work necessary to separate unit area of a liquid from a solid and can be calculated with Dupre’s equation as follows:

\[
W_{ad} = \sigma_{lg} + \sigma_{lg} - \sigma_{ad} \tag{10}
\]

By using Young’s equation, Eq. (5), the work of adhesion can be expressed as:

\[
W_{ad} = \sigma_{lg}(1 + \cos \theta) \tag{11}
\]

The work of adhesion between molten LC steel containing Ti and solid alumina at different experimental temperatures can be obtained with the above Eq. (11) and experimental data.

The results are plotted in Fig. 10 against the Ti content in the molten steel. As shown in the figure, with increasing Ti content, the work of adhesion decreases slightly at 1550°C, stays almost constant when the Ti content is lower than 0.145 mass% and then increases at 1575°C. At 1600°C, the work of adhesion increases with the increase in Ti content.

The influence of Nb or B on the work of adhesion is shown in Fig. 11 against the Nb or B content in the molten LC steel. It is obvious that the work of adhesion between the molten LC steel and solid alumina increases slightly with increasing Nb content at different temperatures. In the range of a B content lower than about 0.05 mass%, the work of adhesion hardly changes, but it increases markedly when B content is higher than about 0.05 mass%. This corresponds to the influence of B in molten LC steel on the contact angle of molten steel on solid alumina.

Assuming the interfacial tension gradient \( K \) is constant, when the thickness of interfacial tension gradient region \( \delta \) is larger than particle diameter \( 2R \), that is, \( \delta > 2R \), Eq. (12) is described by Eq. (13)

\[
F_i = -\frac{8}{3} \pi R^2 K \tag{13}
\]

While interfacial tension gradient \( K \) is shown as the sum of the temperature dependence term \( K_T \) and the solute concentration dependence term \( K_C \), \( K \) can be expressed only by \( K_C \) because \( K_T \) is generally predominant, that is, \(|K_T| << |K_C|\).

\[
K = K_T + K_C = d\sigma/dT \cdot dT/dx + d\sigma/dC \cdot dC/dx \tag{14}
\]

As the first approximation, concentration gradient \( dC/dx \) is written briefly as Eq. (15), assuming that the solute concentration distribution in front of the solidifying interface is linear. \( C/k_0 \) is the solute concentration at the solidifying interface.

\[
dC/dx = (C/k_0 - C)/\delta = (1/k_0 - 1) \cdot C/\delta \tag{15}
\]

Substituting Eqs. (14) and (15) for Eq. (13),

\[
F_i = -\frac{8}{3} \pi R^2 d\sigma/dC \cdot (1/k_0 - 1) \cdot C/\delta \tag{16}
\]

Extracting only the term that depends on the solute component of Eq. (16) and taking the sum total for each solute element \( i \), a new index, which can be used rapidly and quantitatively to predict the difference of the interfacial tension.
gradient force $F_i$ with the steel type using the solute concentration, can be obtained. This index is defined as Mukai-value $M$ and is shown by Eq. (17).

$$M = \sum \frac{d\sigma}{dC_i} \cdot (1/k_i - 1) \cdot C_i = \sum \frac{d\sigma}{dC_i} \cdot M_i \cdot C_i$$ ..........(17)

In the case of gas bubbles in molten steel, measured values on the surface tension of the Fe–$i$ system summarized in the literature are available for estimating the solute concentration dependence of the surface tension of molten steel $\sigma_{\text{Fe}/dC_i}$. In addition, the equilibrium partition coefficient of element $i$ $k_i$ is also summarized in the literature. The above-mentioned treatment of gas bubbles can also be applied to non-metallic inclusions in molten steel.

From the experimental data obtained in this work, $\sigma_{\text{Fe}/dC_i}$ and $M$ at 1 550°C for the molten LC steel containing Ti, Nb or B can be estimated as shown in Table 2. $\sigma_{\text{Fe}/dC_i}$ and $\sigma_{\text{Fe}/dC_i}$ show negative values and decrease with increasing Ti, Nb or B content. That is, the addition of Ti, Nb or B promotes the entrapment of gas bubbles and non-metallic inclusions by the solidifying shell. The effect of Ti, Nb or B on $\sigma_{\text{Fe}/dC_i}$ and $\sigma_{\text{Fe}/dC_i}$ is in order of $B > Ti > Nb$, while the effect of Ti, Nb or B on $M$ for gas bubbles and alumina inclusions is in order of $B > Ti > Nb$.

4.2. Entrapment of Bubbles by the Solidifying Shell in the Continuous Casting of Steel

Fig. 12 shows the fine bubbles in the sub-surface layer of Al-killed LC steel and Ti-added super ultra low-carbon (Ti-SULC) steel slabs. The black dots in the photo are fine gas bubbles. It is obvious that the number and size of the fine bubbles in the sub-surface layer of Ti-SULC steel are larger than those of Al-killed LC steel.

Fig. 13 shows the relation between Mukai-value $M$ for gas bubbles and the number of bubbles in the sub-surface layer of CC slabs. From the experimental data obtained in this work, $\sigma_{\text{Fe}/dC_i}$ and $M$ at 1 550°C for the molten LC steel containing Ti, Nb or B can be estimated as shown in Table 2. $\sigma_{\text{Fe}/dC_i}$ and $\sigma_{\text{Fe}/dC_i}$ show negative values and decrease with increasing Ti, Nb or B content. That is, the addition of Ti, Nb or B promotes the entrapment of gas bubbles and non-metallic inclusions by the solidifying shell. The effect of Ti, Nb or B on $\sigma_{\text{Fe}/dC_i}$ and $\sigma_{\text{Fe}/dC_i}$ is in order of $B > Ti > Nb$, while the effect of Ti, Nb or B on $M$ for gas bubbles and alumina inclusions is in order of $B > Ti > Nb$.

5. Conclusions

The surface tension of molten LC steel containing Ti, Nb or B and the contact angle of molten steel on solid alumina were measured using the sessile droplet method at three experimental temperatures. The following conclusions can be deduced from the present work:

1. The surface tension of molten LC steel containing Ti decreases with increasing Ti content. However, Nb and B are not as surface-active as Ti in molten LC steel. The addition of a small amount of Nb or B to molten LC steels only decreases slightly the surface tension of molten LC steel.

2. The contact angle of the molten LC steel containing Ti on alumina decreases with Ti, Nb or B concentration, but it decreases markedly with B content from 0.050 to 0.0999 mass%.

3. The interfacial tension between molten LC steel containing Ti and alumina decreases with increase in Ti content. The addition of Nb up to about 0.200 mass% to molten LC steel decreases the interfacial tension slightly, but B greatly decreases the interfacial tension with the increase in B content from 0.050 to 0.0999 mass%, before which there is little change in the interfacial tension.

4. From the results in the present work and the discussion on Mukai-value, it can be deduced that fine bubbles are more easily entrapped in the solidifying interface for LC steel containing Ti or B than that containing Nb, while fine alumina inclusions are more easily entrapped in the interface for LC steel containing B than that containing Ti or Nb.

Acknowledgements

The authors would like to sincerely thank Dr. Z. Li, Dr. L. Fang, Dr. T. Matsushita and Dr. K. Wasai for their help.

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**Appendix.**

The results obtained by other researchers for Fe–O system are given in Fig. A-1 as a comparison with the present measurement. As can be seen in Fig. A-1, the surface tension for molten low carbon steel with less oxygen is high in the present work and that with 0.0241 mass% oxygen decreases markedly. The results in the present measurement are in good agreement with those obtained by Zhu et al., Kasama et al., and Jimbo et al. and those at low oxygen content end obtained by Takiuchi et al. and Tszin-Tan et al. and Ershov et al. and Tszin-Tan et al.

![Fig. A-1. Surface tension of molten Fe–O alloys.](image-url)