Decomposition of CaCO₃ in Molten Borate and Its Effect on Slag Foaming Behavior

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(Received on November 12, 1999; accepted in final form on February 2, 2000)

A model for thermal composition of CaCO₃ in Na₂B₄O₇ molten slag is presented in the paper. The experimental results show that the size of CaCO₃ particle and CaO content in slag have effect on foaming by gas inside the slag, and these effects are all dependent on the decomposition behavior of CaCO₃ in molten slag. Therefore, the foaming index, \( \Sigma \), which is measured with bubbling, cannot be employed to evaluate the stability of foams from gas inside the slag.

KEY WORDS: slag foaming; calcium carbonate; thermal decomposition; model; sodium borate melt; foam; foaming height; calcia.

1. Introduction

For recent ten years, slag foaming phenomena have been investigated and reported in progressing quantity, which attributes to the innovation and development of new technologies and process for iron and steel making. After R. J. Fruehan and his collaborators published a series of papers from 1989 and introduced foaming index, based on the experimental results of slag foaming by the gas injection at laboratory, many researchers started to investigate this phenomena by the way of bubbling at laboratory and to employ foaming index to evaluate foaming. However, most slag foaming phenomena occur in metallurgical practice by gas bubbles from thermal decomposition of carbonate minerals. Considering that bubbles by chemical reactions are of smaller initial size and of lower initial kinetic energy, they may have more resident time in slag. The foaming by chemical reactions and that by gas injection may be under different mechanism. So the investigation on foaming by chemical reactions should be conducted. Some early work has been done in which it was discussed whether foaming index was valid for most cases esp. for the foaming by chemical reactions. With limestone and dolomite as the main component of foaming agent, slag foaming technique has been developed and adopted for intensive refining in LF process and EAF operation at reduction period demand slag foaming by gas bubbles from thermal decomposition of carbonate minerals. Considering that bubbles by chemical reactions are of smaller initial size and of lower initial kinetic energy, they may have more resident time in slag. The foaming by chemical reactions and that by gas injection may be under different mechanism. So the investigation on foaming by chemical reactions should be conducted. Some early work has been done in which it was discussed whether foaming index was valid for most cases esp. for the foaming by chemical reactions. With limestone and dolomite as the main component of foaming agent, slag foaming technique has been developed and adopted for intensive refining in LF process and EAF operation at reduction period.¹²¹ It has been reported in many literature that the component and physico chemical properties of slag affect slag foaming.³⁴ but few paper on thermal decomposition of carbonate minerals in molten slag has been published, neither has work on the interactivity between the thermal decomposition and slag foaming.

The molten slag system of Na₂B₄O₇–CaO was used to simulate metallurgical slags for foaming experiments partially because the former has lower melting point than the latter.

2. Model for Thermal Decomposition of Carbonate in Molten Slag

The thermal decomposition of carbonate has been studied for nearly half a century.⁵ And the study has been conducted completely on thermal decomposition rate of limestone lump and limestone fine in the air or under vacuum,⁶ which reveals that the decomposition undergoes three primary steps: heat transfer from outside to particle inside, chemical reaction of thermal decomposition and the outward diffusion of reaction product CO₂. The research by Narsimhan⁷ points out that heat transfer is the limiting step for whole decomposition of limestone. Based on the model for thermal decomposition by Narsimhan, for the sake of quantitative estimation, approximation is assumed for the decomposition conditions as following

(1) Sphere particle of CaCO₃ turns into CaO without change of volume;
(2) The temperature at the surface of sphere particle of CaCO₃ remains at decomposition temperature \( T_d \) during decomposition process, and the heat reaching decomposition interface would be completely consumed by the endotherm of decomposition of CaCO₃;
(3) The temperature at the surface of CaCO₃ particle reaches the same temperature of melt as soon as the particle is added into the melt.

2.1. Model for Thermal Decomposition with CaO Shell Undissolved

At any time \( t \), CaCO₃ sphere with diameter of \( r \) surrounded by the CaO shell with thickness of \( R-r \), the tem-

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The decomposition rate of CaCO₃ can be described as

\[
q_i = 4\pi R^2 \alpha (T_i - T) \quad \text{..................(1)}
\]

the heat flux that reaches the decomposition interface \( r \) is

\[
q_i = \frac{4\pi K_e (T - T_d)}{1 - \frac{r}{R}} \quad \text{..................(2)}
\]

combining Eq. (1) and Eq. (2), it can be formulated as

\[
T = \frac{rK_e T_d + R(R - r)\alpha T_i}{rK_e + R(R - r)\alpha} \quad \text{..................(3)}
\]

substituting Eq. (3) into Eq. (2), it becomes

\[
q_i = \frac{4\pi R^2 \alpha (T_i - T_d)(r/R)}{(r/R) + (R\alpha / K_e)(1-r/R)} \quad \text{..................(4)}
\]

When fluid flows around a single sphere, the average coefficient of heat transfer can be written into equation of dimensionless numbers as follows

\[
Nu = 2 + 0.016Re^{1/2} Pr^{1/3} \quad \text{..................(5)}
\]

For the sake of simplification, fluid is assumed still, so \( Nu = 2 \). And because \( Nu = \alpha d / \lambda \), the coefficient of thermal transmission can be treated as constant, with \( \alpha = \lambda / R \), so Eq. (4) can be rewritten as

\[
q_i = \frac{4\pi R\lambda (T_i - T_d)(r/R)}{r/R + (\lambda / K_e)(1-r/R)} \quad \text{..................(4')}\]

The decomposition rate of CaCO₃ can be described as

\[
-\frac{dW}{dt} = -\frac{\rho}{M_i} \frac{dr}{dt} \quad \text{..................(6)}
\]

According to the assumption stated above, the following equation can be obtained for heat balance

\[
-\frac{dW}{M_i dt} \Delta H_i = q_i \quad \text{..................(7)}
\]

where

\[
\Delta H_i = \Delta H_i + \int_{T_f}^{T_i} C_d dT.
\]

The change of enthalpy by change of temperature of decomposition product is ignored because melt temperature \( (T_f) \) is close to the decomposition temperature \( (T_d) \) of CaCO₃ under the condition of \( p_{CO_2} = 1 \) atm. Combining Eqs. (4'), (6) and (7),

\[
-\frac{\rho}{M_i} \frac{dr}{dt} \Delta H_i = \frac{R\lambda(T_i - T_d)(r/R)}{r/R + (\lambda / K_e)(1-r/R)} \quad \text{..................(8)}
\]

Making \( r' = r/R \), integrating Eq. (8), the time that to decompose CaCO₃ to position \( r \) would take can be expressed as

\[
t = \beta \left[ 1 + \frac{1}{3} \frac{\lambda}{K_e} \right] \left[ \beta \left( \frac{1}{2} \frac{\lambda}{K_e} r' + \frac{1}{3} \left( 1 - \frac{\lambda}{K_e} \right) r'^3 \right) \right] \quad \text{..................(9)}
\]

where

\[
\beta = \frac{\rho \Delta H_i R^2}{M_i \lambda (T_i - T_d)}.
\]

Define \( t_i \) as the whole decomposition time, i.e., when \( r = R \) or \( r' = 1 \), \( t = t_i \), then

\[
t_i = \beta \left[ 1 + \frac{1}{3} \frac{\lambda}{K_e} \right] \quad \text{..................(10)}
\]

### 2.2. Model for Thermal Decomposition with CaO Shell Dissolved Completely

If there is no CaO shell during decomposition of CaCO₃, the heat flux from melt to decomposition interface can be always written as

\[
q_i = 4\pi r^2 \alpha (T_i - T_d) \quad \text{..................(11)}
\]

Because the heat reaching decomposition interface of CaCO₃ is equal to the heating effect of decomposition reaction, from Eqs. (6), (7) and (11), the following relationship could be obtained

\[
-\frac{\rho}{M_i} \frac{dr}{dt} \Delta H_i = \alpha (T_i - T_d) \quad \text{..................(12)}
\]

where coefficient of heat transfer is not constant yet, according to the simplified conditions mentioned above and substituting \( \alpha = \lambda / r \) into Eq. (12), then

\[
-\frac{\rho}{M_i} \frac{dr}{dt} \Delta H_i = \lambda (T_i - T_d) \quad \text{..................(13)}
\]

Making \( r' = (r/R) \), integrating Eq. (13) from \( R \) to \( r \), the time that to decompose CaCO₃ to any position \( r \) would take is got

\[
t = \frac{\rho \Delta H_i R^2}{2M_i \lambda (T_i - T_d)}(1-r^2) = \frac{\beta}{2}(1-r^2) \quad \text{..................(14)}
\]

So, with the model of CaO shell dissolved completely, the
so it can be supposed that besides the CaCO3 and that of CaO is noticeable, so the CaO shell mated from Eqs. (16) and (17).

the two decomposition regimes is of 4 times, which is estimated to measure their decomposition time in two differ-
tent melt, and the diameters are $\phi 0.005$ m, $\phi 0.008$ m, $\phi 0.010$ m and $\phi 0.015$ m, respectively. The time that to decompose sphere CaCO3 particle with different size takes can be theoretically estimated from Eqs. (16) and (17), from which curve a) and curve b) were plotted in Fig. 2, respectively. The eight points in Fig. 2 were plotted according to experimental results. As the eight points are located within the region surrounded with curve a) and b), the real decomposition behavior can be characterized with the model between the two extreme decomposition regimes. The four points marking the decomposition in pure Na2B4O7 are closer to curve a) while the other four points marking that in Na2B4O7–3%CaO are located some more centrically in the region surrounded with curve a) and b). So it may be interpreted that the decomposition behavior in pure borate melt is close to the situation described by the model without CaO shell, because product CaO can dissolve in the melt when there is no CaO in borate melt. When there is some content of CaO in the borate melt, it would take some time to dissolve the product CaO shell, so the decomposition performance tends towards the situation described by the model with CaO shell.

The experimental results show that under the experimen-
tal conditions stated in the paper the decomposition process of CaCO3 can be described as the model with CaO shell.

4. Experimental Results and Discussion

4.1. Thermal Decomposition Behavior of a Single Carbonate Particle in Molten Slag

Marble sphere of four different diameters were experimented to measure their decomposition time in two differ-

| Symbo | $C_p=a+b\times10^{-2}T+c\times10^{-2}T^{-2}$ | $\Delta H_d$ | $\lambda$ | $K_a$ | $\rho$ | $M_t$ | $T_i$ | $T_f$ | $R$ |
|-------|---------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| Data  | 104.52  | 21.92  | $-25.94$ | 161300 | 7.00   | 0.69   | 2700   | 100    | 1171   | 1198   |
| Unit  | J/K mol | J/K$^2$ mol | J/mol | W/m K | W/m K | Kg/m$^3$ | K | K | m |
| Source | Ref. 10 | Ref. 10 | Ref. 8 | Ref. 9 | Ref. 11 | Ref. 10 | Ref. 10 | Ref. 10 | |

* According to experimental data.

2.3. Determination of Parameters for the Model

The thermophysical parameters verifying the model for CaCO3 thermal decomposition are listed in Table 1.

Substituting data in Table 1 into Eq. (10) and Eq. (15), respectively, Eq. (10) and Eq. (15) would become into Eq. (16) and Eq. (17)

$$t_2=\beta/2 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (15)$$

The difference between the decomposition time under the two decomposition regimes is of 4 times, which is estimated from Eqs. (16) and (17).

Actually, the difference between the molar volume of CaCO3 and that of CaO is noticeable, so the CaO shell would become porous after CaCO3 decomposed, and thus the value of heat conductivity $K_a$ would be lower than that from literature. So it can be supposed that besides the temperature, the morphological factor of decomposing product CaO and dissolution behavior of CaO affect the decomposition rate of limestone in melt.

3. Experiment

CaCO3 was decomposed in Na2B4O7–CaO melt in a crucible which was heated in a electric resistance furnace at the temperature of 925±5°C. The slag was charged in the graphite crucible with inner size $0.04\times0.12$ M. The natural marble, with CaCO3 94.4 wt%, was prepared to spheres with different diameter and was bored hollow with a fine hole centrally, so the marble sphere can be hung at an end of a Pt–Rh wire. The marble spheres were submerged into the melt and the time from immersing to whole decomposition was measured. The foaming experiments were conducted under the same conditions. After the temperature of the molten slag reaches the preset value, 0.004 kg marble, 5 wt% of melt, was added into the slag to foam. The foaming height of slag was measured with a molybdenum wire every 30 or 60 s till the foams wholly disappeared.

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the foams clinging to the marble block. In the SEM microphotograph of the specimen, which was a φ 0.015 m sphere marble submerged for 10 min in the Na₂B₄O₇–CaO melt, analysis with probe shows that at point 2 and point 3, no sodium element was found while at point 1 and point 4 sodium was found. Its content is 3.42 wt% and 4.18 wt%, respectively, as shown in (b) of Fig. 3. So in Fig. 3(b), the part marked point 2 and 3 was undecomposed marble. The part marked point 1 and 4 was product CaO, as the sodium element attributes to infiltration of Na₂B₄O₇ into porous CaO shell. Point 4 is near the melt, while point 1 is near the hole in sphere.

4.2. The Effect of Marble Size on Slag Foaming

Experiment was carried out to foam pure Na₂B₄O₇ melt with marble sphere of same mass but different size, and the result is plotted in Fig. 4. In Fig. 4 foaming height of melt is plotted against foaming time, and obviously it is related to the decomposition time of carbonate. For the sake of evaluating the foams life from chemical reactions, the authors presented average foams life as criterion, defined as

\[
\tau = \frac{\int_0^t \Delta h dt}{\dot{Q}}
\]

The average foams life of experiments with 0.003 m and 0.005 m sized particle can be calculated from Eq. (18), with the experimental data shown in Fig. (4), and results are 295.8 s and 264.6 s, respectively. Although the average foams life from the two size foamer are not of much contrast, the former makes 1.67 times foaming height as high as the latter makes, but total foaming time of the former is less one fourth than that of the latter. Figure 5 shows that small-sized foamer makes higher foaming layer but shorter foams lasting time, while large-sized foamer makes thinner foaming layer but longer foams lasting time. If both the proper layer thickness and foams lasting time would be hoped to obtain, the size of foamer should be classified into several grades, and the percentage of each grade in the foamer should be apportioned well.

4.3. The Influence of Slag Content on Foaming by Chemical Reactions

In literature, a) foaming index was employed to evaluate
the foaming index, $\Sigma$, could be employed to evaluate the foamability and foams stability or not should be investigated further, not only because foaming index is not a intrinsic property of slag related to the simple properties of slag (density, viscosity and surface tension of slag, etc.), also because the factors influencing decomposition of foamer would impact the slag foaming. In order to compare the average foams life with foaming index, eight marble particles, weighing 0.004 kg, were added into molten salt containing different concentration of CaO, and experimental result was shown in Fig. 5. Additionally, the foaming index for above melt system was measured by bubbling with argon, and the comparison of average foams life with foaming index for the same molten system was implemented in Table 2. It can be proved clearly from Table 2 that slag component exerts little effect upon foaming index, but it makes foaming behavior by foamer vary much. This is explained from two sides. On one hand, when CaO content in slag is increased, the CaO shell produced from the decomposition of CaCO$_3$ dissolves slow, thus CaCO$_3$ core surrounded by CaO shell decomposes also slow because of the porous CaO shell as a larger thermal resistance. On the other hand, the thicker the CaO porous shell, the smaller the bubble size of CO$_2$ is released, as shown in (c) of Fig. 3. The initial size of these bubbles is of one or two order less than that by gas injection, so the foams stabilizes much. Besides these, whether the change of surface tension gradient at inner film of the bubbles during CaO dissolving, known as Marangoni Effect, would stabilize the foams or not, should be studied further.

5. Conclusions

(1) The decomposition process of CaCO$_3$ in molten slag can be characterized by the heat transfer model with limiting step. The decomposition time of sphere marble is experimentally measured between the two calculated values from model with CaO shell and without it.

(2) It can be achieved to control the foaming height and foaming time caused from decomposition of carbonate by adjusting the size of CaCO$_3$.

(3) Under the conditions of almost the same foaming index, the result that decomposition of CaCO$_3$ is prolonged and size of CO$_2$ bubbles is diminished can be fulfilled by increasing CaO content in melt. Consequently the foams in melt is stabilized.

Table 2. The change of $\Sigma$ and $\tau$ due to CaO concentration in Na$_2$B$_4$O$_7$–CaO melts.

| Mole fraction of CaO (x) (J/mol) | 0    | 0.091 | 0.167 | 0.231 |
|---------------------------------|-----|------|------|------|
| Foaming index $\Sigma$ (s)      | 1.02| 1.32 | 1.16 | 1.27 |
| Foaming life $\tau$ (s)         | 4.67| 9.91 | 26.24| 41.66|

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China under Grant No. 59574026.

Nomenclature

$A$: Cross-sectional area of crucible (m$^2$)

$C_p$: Molar heat capacity of CaCO$_3$ (J/K·mol)

$d$: Diameter of marble sphere (mm)

$\Delta H_d$: Decomposition heat of CaCO$_3$ (J/mol)

$\Delta H_t$: Total change of heat of CaCO$_3$ (J/mol)

$\Delta h$: Height increment of melt (m)

$K_e$: Thermal conductivity of CaO (W/m·K)

$M_f$: Molecular weight of CaCO$_3$ (0.100 kg/mol)

$Nu$: Nusselt number

$Pr$: Prandtl number

$Q$: Gas flowrate (m$^3$/s)

$Q_g$: Total gas volume (m$^3$)

$q_i$: Heat flux (W)

$r$: Any radius of CaCO$_3$ (mm)

$R$: Initial radius of CaCO$_3$ sphere (mm)

$r'$: Dimensionless radius (−)

$Re$: Reynolds number

$T$: Temperature of CaO shell (K)

$T_d$: Fluidization decomposition temperature of CaCO$_3$ (K)

$T_t$: Temperature of melt (K)

$\Delta t$: Time (s)

$\Delta \nu_g$: superficial gas velocity (m/s).

$w$: Mass of CaCO$_3$ (kg)

$x$: Molar fraction of CaO (−)

$\alpha$: Coefficient of heat transfer (W/m$^2$·K)

$\lambda$: Heat conductivity of melt (W/m·K)

$\rho$: Density of CaCO$_3$ (kg/m$^3$)

$\Sigma$: Foaming index (s)

$\tau$: Foams lasting time (s)

$\tau$: Average foams life (s)

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