Decomposition of Na_2CO_3 by Interaction with SiO_2 in Mold Flux of Steel Continuous Casting

Jong-Wan KIM, Yong-Deuk LEE and Hae-Geon LEE¹⁾

STS Research Gr., Technical Research Laboratories, POSCO, Pohang, Kyungbuk, 790-785 Korea.

1) Department of Materials Science and Metallurgical Engineering, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Ku, Pohang, Kyungbuk, 790-784 Korea.

(Received on August 11, 2000; accepted in final form on November 20, 2000)

The effect of SiO_2 addition on the decomposition of Na_2CO_3 was investigated using the thermo-gravimetric and differential scanning calorimetric method (TG-DSC). Addition of SiO_2 greatly enhanced the decomposition of Na_2CO_3 . The main decomposition reaction began to take place at a eutectic temperature of the Na_2O – SiO_2 system (800°C). The initial decomposition product was identified as Na_2SiO_3 , irrespective of the mixing ratio of Na_2CO_3 to SiO_2 . The governing reaction of the decomposition was concluded to be $\text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_3(\text{s}) + \text{CO}_2(\text{g})$. The decomposition rate was independent of the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixing ratio until either one has completely been exhausted and hence was not available any more for the above reaction. If surplus Na_2CO_3 exists after formation of Na_2SiO_3 by reacting with all SiO_2 , the remaining Na_2CO_3 decomposes partly by reacting with Na_2SiO_3 to form $\text{Na}_6\text{Si}_2\text{O}_7$ and partly by thermal self-decomposition. A liquid layer that was formed at the carbonate/additive interface facilitated the decomposition of the carbonates. The melting behavior of a mold flux was greatly influenced by the lowest eutectic temperature that a mold flux system can exhibit. The apparent activation energy of the decomposition of Na_2CO_3 in existence with SiO_2 was estimated to be $426 \text{ kJ} \cdot \text{mol}^{-1}$.

KEY WORDS: mold flux; Na_2CO_3 ; SiO_2 ; decomposition; activation energy.

1. Introduction

Mold flux is of importance in the continuous casting of steels. Lubrication of the cast surface against the mold wall, control of heat transfer between the mold and cast body, insulation of the molten steel pool in the mold, protection of liquid steel against reoxidation, and absorption of inclusions are among some of the important functions of the mold flux. Tight control of the melting behavior and physico-chemical properties of the mold flux are therefore essential for the production of quality cast.

Na_2O is widely used as a fluxing material and added 1 to 20 wt%¹⁾ to control the melting behavior and viscosity of the mold flux. In general, Na_2O is added as carbonate (Na_2CO_3), which would decompose during melting of the mold flux. Recently, it was reported that the increase in the melting rate of the mold flux by the addition of carbonates such as Na_2CO_3 and Li_2CO_3 is due to an increase in the thermal conductivity of the mold flux by gases generated during decomposition of the carbonates.²⁾ It has also been reported that, if the amount of carbonates is excessive, turbulence in the mold is caused by virtue of an intense evolution of gases. In order to make the most of the beneficial effects of the carbonates, therefore, it is essential to understand in detail how the carbonates interact with other components in the mold flux and hence influence the melting behavior of the mold flux. Systematic studies on the de-

composition of carbonates such as Na_2CO_3 and Li_2CO_3 in existence with SiO_2 in the mold flux system are few.³⁾ Only some studies on the reaction between Na_2CO_3 and SiO_2 in the glass-making system were reported.^{4,5)}

In the present study, an attempt has been made to elucidate the decomposition behavior of Na_2CO_3 by interaction with SiO_2 that exists in the mold flux.

2. Experimental

The chemical composition of the materials used in the present study is given in **Table 1**. A thermal analyzer equipped with both thermo-gravimetric (TG) and differential scanning calorimetric (DSC) functions was employed, which enabled the simultaneous analysis of TG and DSC

Table 1. Chemical composition of the materials.

	(mass %)			
	Na_2CO_3	SiO_2	Carbon black	Mold powder
CaO	–	–	–	38
SiO_2	–	96.3	–	30
Al_2O_3	–	–	–	7
Na_2O	56	–	–	9
Li_2O	–	–	–	–
Total C	11.1	0.3	99.9	3.4
CO_2	40.7	1.0	–	–

Fig. 1. TG-DSC results with pure Na_2CO_3 and mixture of Na_2CO_3 and SiO_2 .

Fig. 2. Changes in the rate of mass loss and heat flow during TG-DSC analysis of Na_2CO_3 mixed with SiO_2 (m : total mass, t : time).

with a detection accuracy of $\pm 1 \mu\text{g}$. All the decomposition experiments were carried out in an inert atmosphere by flowing purified argon gas at the rate of $5 \times 10^{-5} \text{ m}^3 \cdot \text{min}^{-1}$. The sample mass was in the range of 15 to 50 mg depending on the experimental condition. A number of different mixing ratios of Na_2CO_3 to SiO_2 were employed to investigate the effect of the ratio on the decomposition behavior. The decomposition of pure Na_2CO_3 and Na_2CO_3 mixed with carbon was also investigated for the purpose of comparison. Alumina powder was used as reference material. Both the sample and reference were contained in a platinum crucible (5 mm ID and 6 mm L). The samples were heated up to a desired temperature at the heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Once the temperature had reached the desired level, the samples in the crucible were lowered to the bottom of the furnace and immediately quenched by blowing helium gas. Some samples were subjected to XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope) analyses for phase determination. For these analyses samples were heated in a vertical tube furnace under otherwise the same experimental conditions as TG-DSC and then quenched. The temperature was accurately controlled using a thermocouple positioned just above the sample.

3. Results and Discussion

3.1. Observations

Figure 1 is a typical TG-DSC results for the decomposition of Na_2CO_3 mixed with SiO_2 . For the purpose of comparison, the decomposition behavior of pure Na_2CO_3 is also given in this figure. It shows a change in the mass of the sample and the heat flow over time (10°C increment is equivalent to one minute). It is clearly seen that there is a vast difference in the decomposition behavior of Na_2CO_3 between the two cases. Na_2CO_3 mixed with SiO_2 begins to decompose at the temperature of 770°C , whereas pure Na_2CO_3 hardly decomposes at this temperature, and the decomposition rate is extremely slow even after melting point $850^\circ\text{C}^{(6)}$ (see the endothermic peak in Fig. 1). Moreover, the rate of decomposition of Na_2CO_3 mixed with SiO_2 increases

very rapidly by increasing the temperature. Figure 2 shows the change in the rate of mass loss (dm/dt) and the heat flow during TG-DSC analysis of Na_2CO_3 mixed with SiO_2 . The rate of mass loss reaches the maximum level when the temperature approaches the melting point of Na_2CO_3 , which corresponds to the peak of the curve of the heat flow. Figures 1 and 2 also show that the decomposition of Na_2CO_3 due to the reaction with SiO_2 is complete just after the temperature has reached the melting point of Na_2CO_3 . It is now obvious that existence of SiO_2 greatly enhances the decomposition of Na_2CO_3 .

Reactions that are responsible for the decomposition of Na_2CO_3 in a usual mold flux system include:

In order to examine which of the above reactions would dominate the decomposition of Na_2CO_3 in a mold flux system which contains both carbon and SiO_2 , a separate experiment was carried out by using a mixture of Na_2CO_3 and carbon black, with results being given in Fig. 3. It is clear that the decomposition of Na_2CO_3 mixed with SiO_2 occurs at much lower temperatures and is nearly complete by the time decomposition of Na_2CO_3 mixed with carbon black is just beginning to take place. The above observations confirm the view that the decomposition of Na_2CO_3 occurs predominantly by the interaction with SiO_2 rather than with carbon. In order to examine the effect of the relative amount of SiO_2 on the decomposition of Na_2CO_3 , experiments were carried out with samples of a number of different mixing ratios of Na_2CO_3 to SiO_2 , i.e., $\text{Na}_2\text{CO}_3/\text{SiO}_2$ in molar ratio of 1.0/0.0, 1.0/0.5, 1.0/1.0, 1.0/1.5, and 1.0/2.0, and results are given in Fig. 4. It is seen that, except the case of no addition of SiO_2 , the mass loss varied with temperature for each mixing ratio follows a nearly identical path until the temperature reaches the point indicated by an arrow in the figure. In other words, the decomposition of

Fig. 3. Changes in the rate of mass loss due to decomposition of Na_2CO_3 : (1) Pure Na_2CO_3 , (2) Na_2CO_3 with carbon black, (3) Na_2CO_3 with SiO_2 .

Fig. 4. Mass loss of Na_2CO_3 - SiO_2 mixtures of different mixing ratios during heating.

Na_2CO_3 in coexistence with SiO_2 is governed by an identical reaction, irrespective of the relative amount of SiO_2 until the temperature indicated by the arrow reaches. **Figure 5** compares the mass loss observed until the temperature reaches the point indicated by an arrow in Fig. 4 with that calculated assuming the loss being governed by the reaction of Eq. (3). It is seen that the observed and calculated results are in good agreement with each other. Therefore the mass balance analysis confirms that the governing reaction is the one represented by Eq. (3). It might be argued that there might also be the possibility of forming other types of silicates such as $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ or $2\text{Na}_2\text{O} \cdot \text{SiO}_2$. To identify the phase of decomposition products, XRD analyses have been carried out with samples quenched after the decomposition reaction had been complete. Quenching temperatures were 900, 870 and 930°C for 1.0/1.0, 1.0/2.0 and 1.0/0.5 molar ratios of Na_2CO_3 / SiO_2 , respectively. The results are given in **Fig. 6** in which no silicates other than $\text{Na}_2\text{O} \cdot \text{SiO}_2$ are found up until the

Fig. 5. Comparison of observed mass loss with the mass loss calculated assuming Eq. (3) being the governing reaction.

Fig. 6. Results of X-ray diffraction analysis of products formed by decomposition of Na_2CO_3 mixed with SiO_2 .

temperature has reached the specified level for each mixing ratio. For the case of 1.0/0.5 molar ratio of Na_2CO_3 / SiO_2 which shows a sharp change in decomposition rate (see Fig. 4), a separate investigation was undertaken, and results are discussed in Sec. 3.3.

3.2. Thermodynamic Predictions

A number of different reactions other than that represented by Eq. (3) can be thought to occur in a system comprising Na_2CO_3 and SiO_2 . These include

Standard free energy changes of the reactions⁷⁾ represented by Eqs. (1) to (7) are plotted against temperature in Fig. 7. The change in slope in a free energy line indicates phase transformation of a constituent (either a reactant or product) involved in the reaction. It is seen that the reaction which is most feasible to occur from a thermodynamic point of view is obviously the one represented by Eqs. (3) and (4). This prediction is in accordance with the observation in that Na_2SiO_3 is the only type of silicate found in the

Fig. 7. Standard free energy changes of various reactions in the system comprising Na_2CO_3 and SiO_2 .

experiments regardless of the mixing ratio of Na_2CO_3 to SiO_2 (Fig. 6). No formation of $\text{Na}_2\text{Si}_2\text{O}_5$ in the present study is postulated to be due to a kinetic reason, *i.e.*, the formation reaction being substantially slow and/or the activation energy, for the reaction being much too high, for instance. The above free energy analysis is in fact applicable only when the system is under a thermodynamic equilibrium and all species are in their standard states, but the system of the present experimental study, which experiences a rise in temperature at the rate of $10 \text{ K} \cdot \text{min}^{-1}$, is not necessarily in equilibrium at every moment. Moreover, it is seen from Fig. 8⁸⁾ that Na_2SiO_3 should be observed only with the mixing ratio of Na_2CO_3 to SiO_2 being 1.0/1.0, not with other mixing ratios. However, Na_2SiO_3 is the only silicate that is observed in all the mixing ratios up until the temperature reaches $1,000^\circ\text{C}$ in present experiments. One conceivable way that can satisfy all the above observations and discussion is to conclude that the reaction of Eq. (3) is kinetically faster than other reactions, and hence governs the decomposition process of Na_2CO_3 , *viz.*, Na_2SiO_3 forms first at all mixing ratios of $\text{Na}_2\text{CO}_3/\text{SiO}_2$ investigated.

3.3. Reaction Paths

Based on the observations and discussion given above, it is now possible to discuss reaction paths that the system comprising Na_2CO_3 and SiO_2 follows under the conditions prevailing in the present study.

Figure 4 shows that, when a mixture of Na_2CO_3 and SiO_2 is heated continually, the decomposition of Na_2CO_3 begins to occur to an appreciable extent at around 800°C as seen in Figs. 1–4. It is of interest to know that this temperature corresponds to the eutectic point (799°C) of the Na_2O – SiO_2 system (point A in Fig. 8). This coincidence suggests that the main decomposition reaction of Na_2CO_3 begins to take place when a liquid phase of $(\text{Na}_2\text{O} + \text{SiO}_2)$ mixture forms at the $\text{Na}_2\text{CO}_3(\text{s})/\text{SiO}_2(\text{s})$ interface. Once the liquid phase has been formed, the following processes are postulated to proceed simultaneously:

(a) Dissolution of SiO_2 into the liquid phase at the $\text{SiO}_2/$

Fig. 8. Equilibrium phase diagram of the Na_2O – SiO_2 binary system.

Fig. 9. SEM and EPMA analysis of the initial material (a) and the sample quenched in the middle of decomposition (b).

liquid interface,

(b) Formation of $\text{Na}_2\text{SiO}_3(\text{s})$ at the Na_2CO_3 /liquid interface,

(c) Dispersion of $\text{Na}_2\text{SiO}_3(\text{s})$ due to CO_2 gas generation,

(d) Dissolution of a portion of $\text{Na}_2\text{SiO}_3(\text{s})$ into the liquid,

(e) Mass transfer in the liquid phase

where the round bracket indicates the liquid solution phase, the subscript N/L represents the interface between Na_2CO_3 and the liquid phase, and the subscript S/L stands for the interface between SiO_2 and the liquid phase.

The rate of each process in the above will be enhanced with temperature, as is clearly seen in Figs. 3 and 4. Formation of Na_2SiO_3 and subsequent dispersion is confirmed in Fig. 9, which shows both the starting materials and the sample quenched in the middle of the decomposition process. A liquid layer around the SiO_2 particles is clearly visible as indicated by "A" in the figure. The EPMA line analysis shows that in the region indicated by "A" concentration gradients of both sodium (Na) and silicon (Si) are being developed, which indicates these oxides of Na_2O and SiO_2 , respectively, being transported in the opposite di-

Fig. 10. TG-DSC results with the mixture of Na_2CO_3 and SiO_2 at the mole ratio of 1/1.

rection to each other. The above processes will continue to proceed until either SiO_2 or Na_2CO_3 has been completely exhausted. In the case of the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixing molar ratio of 1.0/1.0 which is the exact stoichiometric ratio for the reaction of Eq. (3), the decomposition product should be Na_2SiO_3 only. As seen in Fig. 6(a), the majority of the product is indeed Na_2SiO_3 . However, a small amount of SiO_2 is also identified. This can be explained in conjunction with the decomposition curve for the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ molar ratio of 1.0/1.0 in Fig. 4. In this case, as the decomposition approaches completion, the amount of solid Na_2SiO_3 increases at the expense of the liquid phase and hence the transfer of Na_2O and SiO_2 in the liquid phase is hindered. This explains the rate of decomposition being sluggish toward completion of the decomposition (Fig. 4) and the small residual amount of SiO_2 is left (Fig. 6). Further evidence of the formation of Na_2SiO_3 was obtained through TG-DSC analysis for the sample of $\text{Na}_2\text{CO}_3/\text{SiO}_2$ molar ratio of 1.0/1.0 as given in Fig. 10. The endothermic peak at 1082°C in the figure corresponds to the melting point of Na_2SiO_3 (see Fig. 8). This suggests that solid Na_2SiO_3 forms in the course of Na_2CO_3 decomposition in existence with SiO_2 and melts when the temperature exceeds its melting point. In cases where the amount of SiO_2 exceeds the stoichiometric requirement of the reaction of Eq. (3), i.e., the molar ratio of SiO_2 to Na_2CO_3 is greater than 1.0/1.0, all the Na_2CO_3 will completely decompose and there will be $\text{SiO}_2(\text{s})$ left afterward. However, as the coexistence of Na_2SiO_3 and SiO_2 is not an equilibrium combination (see Fig. 8), there should be a liquid phase during the course of decomposition, and the amount of the liquid phase should increase as time lapses. Figure 6(b) which shows a glassy phase together with Na_2SiO_3 and SiO_2 confirms the above view, and the existence of the liquid phase to a substantial amount warrants a fast rate of decomposition until the decomposition is complete (see the curves for the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixing ratio of 1.0/1.5 and 1.0/2.0 in Fig. 4). Figure 11 shows the change in the relative amount of each species during the course of decomposition of Na_2CO_3 . It is seen that the amount of Na_2SiO_3 increases at the expense of SiO_2

Fig. 11. Relative amount of each species during the course of decomposition of Na_2CO_3 mixed with SiO_2 .

Fig. 12. Mass loss curves of TG analysis for the decomposition of pure Na_2CO_3 and mixture of Na_2CO_3 (1 mol)+ SiO_2 (0.5 mol).

and Na_2CO_3 as the fraction of the reaction increases.

It was noted earlier that decomposition behavior in the case of 1.0/0.5 mixing ratio of $\text{Na}_2\text{CO}_3/\text{SiO}_2$ showed a sharp change in the decomposition rate, *viz.*, a rapid decomposition rate followed by a much slower rate (see Fig. 4). According to the mass balance calculation (Fig. 5) and XRD analysis (Fig. 6), the point where the rate experiences a sudden change was confirmed to indicate the moment at which SiO_2 in the mixture had been exhausted due to the reaction represented by Eq. (3) and hence the reaction product of Na_2SiO_3 and surplus Na_2CO_3 were left. Careful comparison of the decomposition rate after passing the point with that of pure Na_2CO_3 reveals that further decomposition of $\text{Na}_2\text{SiO}_3/\text{Na}_2\text{CO}_3$ mixture is faster than that of pure Na_2CO_3 (see Fig. 4). This implies that decomposition of Na_2CO_3 in the $\text{Na}_2\text{SiO}_3/\text{Na}_2\text{CO}_3$ mixture does not follow the same path as that of pure Na_2CO_3 . In order to understand the difference, additional decomposition experiment was carried out with an $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixture of 1.0/0.5 molar ratio until the temperature reached 1200°C. The TG

Fig. 13. Results of X-ray diffraction analysis of products formed by decomposition of mixture of Na_2CO_3 (1 mol)+ SiO_2 (0.5 mol).

result is given in Fig. 12. The result of decomposition of pure Na_2CO_3 is also included in this figure for the purpose of comparison. It is clear from this figure that, at the point A which indicates complete exhaustion of SiO_2 in the mixture, the rate of mass loss sharply decreases, but is still faster than that of pure Na_2CO_3 . The rate rises with temperature, but the rising rate is higher for pure Na_2CO_3 . At around 1100°C both rates become the same as each other. In order to identify decomposition products samples were quenched at a number of different temperatures, *viz.*, 870, 930 and 1050°C, and the quenched samples were subjected to XRD analysis, with results being given in Fig. 13. At both 870 and 930°C Na_2SiO_3 and Na_2CO_3 were found, but at 1050°C $\text{Na}_6\text{Si}_2\text{O}_7$ ($3\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) is identified in addition. This suggests that the following reaction (Eq. 13) is operative in the $\text{Na}_2\text{SiO}_3/\text{Na}_2\text{CO}_3$ mixture:

Motzföldt⁹⁾ suggested that the following reaction of Eq. (14) was responsible for the decomposition of pure Na_2CO_3 , based on the observations that the Na_2O content in Na_2CO_3 (I) was in the order of 1 mass%, and Na_2O was not detected in the remaining sample:

With the experimental findings and discussion given above, it is now possible to draw conclusions as follows:

- (1) On heating of an $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixture Na_2CO_3 de-

Fig. 14. TG-DSC results of Na_2CO_3 decomposition in coexistence with spodumene and carbon black.

composes to form $\text{Na}_2\text{O} \cdot \text{SiO}_2$ according to Eq. (3).

(2) If surplus Na_2CO_3 exists after formation of $\text{Na}_2\text{O} \cdot \text{SiO}_2$ with complete exhaustion of SiO_2 , further decomposition of excess Na_2CO_3 occurs according to both reactions of Eqs. (13) and (14) simultaneously. At the initial stage the decomposition occurs dominantly according to Eq. (13) since the decomposition of Na_2CO_3 alone is slow. As the temperature rises, the decomposition rate according to Eq. (14) increases more rapidly and hence the reaction of Eq. (14) becomes dominant. Further evidence of the reaction of Eq. (14) being operative can be found from the mass loss given in Fig. 12: If Eq. (13) were the only reaction that occur, decrease in the mass of the system should stop after losing 32% of its initial value according to the reaction stoichiometry. Continual mass loss beyond this limit in the actual experiment proves that the reaction of Eq. (14) also occurs simultaneously.

3.4. Decomposition in a Mold Flux System

Spodumene ($\text{LiAl}(\text{SiO}_3)_2$) is usually used instead of pure SiO_2 in practical mold fluxes. Carbon is also added for the purpose of melting control. Decomposition behavior of Na_2CO_3 in coexistence with $\text{LiAl}(\text{SiO}_3)_2$ and carbon was investigated using the same technique as that for Na_2CO_3 mixed with SiO_2 , with the results being given in Fig. 14. It is seen that the decomposition begins somewhere between 550 to 600°C, and is complete before the temperature reaches 800°C. Decomposition of Na_2CO_3 with spodumene begins and ends at lower temperatures than that with pure SiO_2 . In coexistence with spodumene, the decomposition of Na_2CO_3 will form a quarternary system of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}$. Although the phase relationship of this system is not readily available, it is of interest to know that the lowest eutectic points of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{SiO}_2-\text{Li}_2\text{O}$ ternary systems are 732¹⁰⁾ and 585°C,¹¹⁾ respectively. From the comparison with the eutectic point of 799°C for $\text{Na}_2\text{O}-\text{SiO}_2$ binary system, it is obvious that the temperature of a liquid phase formation at Na_2CO_3 /spodumene interface is lower than that at the Na_2CO_3 / SiO_2 interface. This is further evidence that the formation of a liquid phase at

Fig. 15. Kinetic analysis of thermal decomposition of Na_2CO_3 with SiO_2 .

the carbonate/additive interface facilitates the decomposition of Na_2CO_3 . In summary, the lowest eutectic temperature of a mold flux system is considered to be an important factor which controls the melting behavior of the mold flux.

3.5. Activation Energy of Decomposition

The Freeman–Carroll method¹²⁾ is employed in the analysis of TG-DSC experimental data. In this method, the rate expression for disappearance of a reactant from the mixture is assumed to be

$$-\frac{dX}{dt} = kX^n \quad \text{.....(15)}$$

where, X is the amount of the reactant at time t , k is the specific rate constant, n is the empirical order of irreversible reaction with respect to reactant.

It is assumed that the specific rate constant can be expressed by a simple Arrhenius equation

$$k = Ae^{-E/RT} \quad \text{.....(16)}$$

where A is the frequency factor, E is the apparent activation energy, R is the gas constant, and T is the absolute temperature.

From the Eqs. (15) and (16), Freeman and Carroll derived the following equation:

$$-\frac{E}{2.3R} \Delta \left(\frac{1}{T} \right) = -n + \frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r} \quad \text{.....(17)}$$

$$W_r = w_c - w \quad \text{.....(18)}$$

where w_c is the weight loss at the completion of a reaction, and w is the total weight loss up to time, t .

By plotting Eq. (17), the order of reaction and the activation energy for the reaction of interest can be obtained. The relationship between $\Delta \log(dw/dt)/\Delta \log W_r$ term and $\Delta T^{-1}/\Delta \log W_r$ term for the decomposition of Na_2CO_3 with SiO_2 given in Fig. 4 is shown in Fig. 15. The result shows a reasonably good linear relationship. The activation energy of

the decomposition reaction of Na_2CO_3 with SiO_2 is estimated to be $426 \text{ kJ} \cdot \text{mol}^{-1}$. This value is much higher than the reported activation energy of $246 \text{ kJ} \cdot \text{mol}^{-1}$ for thermal decomposition of Na_2CO_3 ³⁾ and $189 \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction of Na_2CO_3 with bastnasite concentrate.¹³⁾ The high activation energy of Na_2CO_3 decomposition with SiO_2 implies that the rate controlling step of the decomposition of Na_2CO_3 with SiO_2 should be the one whose rate is greatly enhanced by thermal energy. The experimental observations summarized in the following leads to the conclusion that, among the elementary steps for Na_2CO_3 decomposition represented by Eqs. (8) to (12), the dissolution of SiO_2 into the liquid phase, Eq. (8), is most likely to be the rate controlling step:

(1) The reaction path of the present experimental system is far removed from an equilibrium path.

(2) The decomposition product is always Na_2SiO_3 .

(3) The liquid phase is stirred by the CO_2 gas generated by the decomposition reaction. The value of the activation energy given above is then the one for dissolution of $\text{SiO}_2(\text{s})$ into the Na_2O – SiO_2 liquid solution.

4. Conclusions

The effect of SiO_2 addition on the decomposition of Na_2CO_3 was investigated using the thermo-gravimetric and differential scanning calorimetric method (TG-DSC). The findings are summarized in the following:

(1) The decomposition of Na_2CO_3 is greatly enhanced by the addition of SiO_2 . The major decomposition reaction begins to take place at the eutectic temperature in Na_2O – SiO_2 system (800°C).

(2) The initial decomposition product is Na_2SiO_3 irrespective of the mixing ratio of Na_2CO_3 to SiO_2 . Thus, the governing reaction of the decomposition is

This reaction completes at near the melting point of Na_2CO_3 .

(3) The decomposition rate is independent of the $\text{Na}_2\text{CO}_3/\text{SiO}_2$ mixing ratio until either one has completely exhausted and hence is not available for the above reaction.

(4) If surplus Na_2CO_3 exists after formation of Na_2SiO_3 by reacting with all SiO_2 , the Na_2CO_3 decomposes partly by reacting with Na_2SiO_3 to form $\text{Na}_6\text{Si}_2\text{O}_7$ and partly by thermal self-decomposition into $\text{Na}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{O}_2(\text{g})$. As the temperature increases, the latter becomes more significant.

(5) An important factor that controls the melting of a mold flux is the lowest eutectic temperature which the mold flux system can exhibit.

(6) The apparent activation energy of the decomposition of Na_2CO_3 in existence with SiO_2 is $426 \text{ kJ} \cdot \text{mol}^{-1}$.

REFERENCES

- 1) J. A. Moore, R. J. Phillips and T. R. Gibbs: *Steelmaking Conf. Proc.*, ISS, Warrendale, PA, **74** (1991), 615.
- 2) M. Kawamoto, K. Nakajima, T. Kanajawa and K. Nakai: *ISIJ Int.*, **34** (1994), 593.
- 3) Y. Nakamura, K. Harashima, Y. Hukuda, N. Tokumitsu and S. Yamamoto: *Tetsu-to-Hagane*, **66** (1980), 2023.
- 4) F. W. Wilburn and C. V. Thomasson: *J. Soc. Glass Technology*, **42** (1958), 158T.
- 5) C. V. Thomasson and F. W. Wilburn: *Phys. Chem. Glass*, **1** (1960), 52.
- 6) O. Knacke, O. Kubaschewski and K. Hesselmann: *Thermochemical Properties of Inorganic Substances*, 2nd ed., Springer-Verlag, Düsseldorf, (1991), 1352.
- 7) Thermo-Calc software package ver. M: RIT, SWEDEN.
- 8) *Slag Atlas*, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 94.
- 9) K. Motzfeldt: *J. Phys. Chem.*, **59** (1955), 139.
- 10) *Slag Atlas*, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 117.
- 11) *Slag Atlas*, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 150.
- 12) E. S. Freeman and B. Carroll: *J. Phys. Chem.*, **62** (1958), 394.
- 13) Liu Zhaogang and Ma Ying: *The Chinese Journal of Non Ferrous Metals*, **8** (1998), 299.