Decomposition of Li$_2$CO$_3$ by Interaction with SiO$_2$ in Mold Flux of Steel Continuous Casting

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

STS Research Group, Technical Research Laboratories, POSCO, Pohang Korea. 1) Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Ku, Pohang 790-784 Korea.

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The effect of SiO$_2$ addition on the decomposition of Li$_2$CO$_3$ was investigated using the thermo-gravimetric and differential scanning calorimetric method (TG-DSC) at temperatures up to 1 000°C. Addition of SiO$_2$ greatly enhanced the decomposition of Li$_2$CO$_3$. The main decomposition reaction began to take place around 600°C, and completed just above the melting point of Li$_2$CO$_3$. The decomposition product was Li$_2$O·SiO$_2$ irrespective of the Li$_2$CO$_3$ to SiO$_2$ mixing ratio as long as both reactants were available. It was ascertained that a liquid layer between Li$_2$CO$_3$ and SiO$_2$ particles formed and facilitated the decomposition reaction. The governing reaction of the decomposition was the reaction between the dissolved Li$_2$CO$_3$ and SiO$_2$ in the liquid layer to form Li$_2$O·SiO$_2$. The decomposition rate was independent of the Li$_2$CO$_3$/SiO$_2$ mixing ratio until either one had been completely exhausted. When excess Li$_2$CO$_3$ existed, it further reacted with the initial product of Li$_2$O·SiO$_2$ to form 2Li$_2$O·SiO$_2$. When SiO$_2$ was found in excess, on the other hand, no further reaction took place. This is attributed to the fact that upon Li$_2$CO$_3$ exhaustion there is no liquid phase available to facilitate further reaction. The apparent activation energy of the decomposition of Li$_2$CO$_3$ in existence with SiO$_2$ is 198 kJ mol$^{-1}$.

KEY WORDS: mold flux; Li$_2$CO$_3$; SiO$_2$; decomposition; activation energy.
2. Experimental

Materials used in the present study are those commercially available for mold flux preparation: Li$_2$CO$_3$ (97.4 mass%) and SiO$_2$ (96.3 mass% with 0.3 mass% C as impurity). The mean sizes of Li$_2$CO$_3$ and SiO$_2$ particles are 20 and 52.4 μm, respectively. The present experimental study was carried out by using a thermal analyzer equipped with both thermo-gravimetric (TG) and differential scanning calorimetric (DSC) functions, which enabled simultaneous analysis of TG and DSC with a detection accuracy of ±1 μg. An inert atmosphere was maintained during the experiment by flowing purified argon gas at the rate of 5×10$^{-3}$ m$^3$/min. The sample mass for each experiment was in the range of 15 to 50 mg depending on experimental conditions. A number of different Li$_2$CO$_3$ to SiO$_2$ mixing ratios were employed to investigate how the ratio affects the decomposition behavior. The decomposition of pure Li$_2$CO$_3$ and Li$_2$CO$_3$ mixed with carbon was also investigated for the purpose of comparison. Al$_2$O$_3$ powder was used as the reference material. Both the sample and reference were held in a platinum crucible (5 mm ID and 6 mm L). The samples were heated up to a desired temperature at a heating rate of 10°C per min. Once the temperature had reached a desired level, samples were immediately quenched by lowering the crucible to the furnace bottom and flowing helium gas over it. Some samples were subjected to XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope) analyses for phase determination.

3. Results and Discussion

3.1. Observations

Figure 1 shows a typical TG-DSC result of the decomposition of Li$_2$CO$_3$ mixed together with SiO$_2$. The decomposition behavior of pure Li$_2$CO$_3$ is also given in the figure for comparison. The figure shows the change of both the mass of the sample and the heat flow over time when it is subjected to continuous heating (10°C per min). It is clear from the figure that the decomposition behavior of Li$_2$CO$_3$ is vastly different between the two cases. Li$_2$CO$_3$ begins to decompose at around 600°C when mixed with SiO$_2$, whereas pure Li$_2$CO$_3$ hardly decomposes at this temperature, and the decomposition rate is quite slow even after melting (see the endothermic peak in Fig. 1). Moreover, the Li$_2$CO$_3$ decomposition rate, when mixed with SiO$_2$, increases very rapidly with increasing temperature. Figure 2 shows the dependence of the rate of mass loss and heat flow on temperature during TG-DSC analysis of Li$_2$CO$_3$ mixed with SiO$_2$ in the Li$_2$CO$_3}$/SiO$_2$ molar ratio=1/1.5. The rate reaches its maximum when the temperature approaches the melting point of Li$_2$CO$_3$. Figures 1 and 2 also show that the decomposition of Li$_2$CO$_3$ is complete just after the temperature has reached the melting point of Li$_2$CO$_3$ (733°C). It is now obvious that existence of SiO$_2$ greatly enhances the decomposition of Li$_2$CO$_3$. Reactions that are responsible for the decomposition of Li$_2$CO$_3$ in a usual mold flux system include:

\[ \text{Li}_2\text{CO}_3 = \text{Li}_2\text{O} + \text{CO}_2(g) \] ..................................(1)

\[ \text{Li}_2\text{CO}_3 + \text{C} = \text{Li}_2\text{O} + 2\text{CO}(g) \] ..................................(2)

In order to examine which of the above reactions would dominate the decomposition of Li$_2$CO$_3$ in a mold flux system which contains both carbon and SiO$_2$, a separate experiment was carried out with a mixture of Li$_2$CO$_3$ and carbon black, and results are given in Fig. 3. It is clear that the decomposition of Li$_2$CO$_3$ mixed with SiO$_2$ occurs at a much lower temperature and is nearly complete by the time the decomposition of Li$_2$CO$_3$ mixed with carbon black is just beginning to take place. The above observations confirm the view that decomposition of Li$_2$CO$_3$ occurs predominantly by its interaction with SiO$_2$ rather than with carbon. In order to examine the effect of the relative amount of SiO$_2$ on Li$_2$CO$_3$ decomposition, experiments were carried out with samples prepared with a number of different Li$_2$CO$_3$ to SiO$_2$ mixing ratios of, i.e., Li$_2$CO$_3$/SiO$_2$ in molar ratios of 1/0.0, 1/0.33, 1/0.5, 1/1.0, 1/1.5 and 1/2.0, and results are given in Fig. 4. It is seen that except the case of non-addi-
tion of SiO₂, the mass loss with time (or temperature) for each mixing ratio follows a nearly identical path until the time reaches the point indicated by an arrow in the figure. In other words, the decomposition of Li₂CO₃ in coexistence with SiO₂ is governed by an identical reaction mechanism, irrespective of the relative amount of SiO₂ until the time indicated by the arrow is reached. Considering compounds to be formed in the Li₂CO₃–SiO₂ system, the reaction represented by Eq. (3) may be rewritten as follows:

\[
\text{Li}_2\text{CO}_3 + \text{SiO}_2 = \text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2(g) \quad \cdots \cdots \cdot (4)
\]

\[
\frac{1}{2} \text{Li}_2\text{CO}_3 + \text{SiO}_2 = \frac{1}{2} \text{Li}_2\text{O} \cdot 2\text{SiO}_2 + \frac{1}{2} \text{CO}_2(g) \quad \cdots \cdots \cdot (5)
\]

\[
2\text{Li}_2\text{CO}_3 + \text{SiO}_2 = 2\text{Li}_2\text{O} \cdot \text{SiO}_2 + 2\text{CO}_2(g) \quad \cdots \cdots \cdot (6)
\]

The amount of sample mass loss due to CO₂ gas evolution will be determined by the reaction that governs: for example, if the decomposition is governed by the reaction of Eq. (4), each mol of SiO₂ will result in the mass loss equivalent to one mol of CO₂. Similarly, the mass loss for a given mol of SiO₂ by Eqs. (5), (6) and (7) will be equivalent to 0.5, 2 and 4 mols of CO₂, respectively. In the present study the initial sample mass was kept at 50 mg throughout the experiment, and hence different molar ratios of Li₂CO₃/SiO₂ give different total as well as individual number of mols of Li₂CO₃ and SiO₂. The actual number of mols and mass of Li₂CO₃ and SiO₂ in the samples in the different mixing ratios are given in Table 1. In Fig. 5 the mass losses observed up until the time reaches the point indicated by the arrows in Fig. 4 are compared with mass losses calculated assuming different reactions being the governing reaction.

\[
4\text{Li}_2\text{CO}_3 + 3\text{SiO}_2 = 4\text{Li}_2\text{O} \cdot 3\text{SiO}_2 + 4\text{CO}_2(g) \quad \cdots \cdots \cdot (7)
\]

\[
\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{Li}_2\text{CO}_3 = 2\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2 \quad \cdots \cdots \cdot (8)
\]

\[
\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{SiO}_2 = \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \quad \cdots \cdots \cdot (9)
\]

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Fig. 3. Changes in the rate of mass loss due to decomposition of Li₂CO₃: (1) pure Li₂CO₃, (2) Li₂CO₃ with carbon black, (3) Li₂CO₃ with SiO₂.

Fig. 4. Mass loss of Li₂CO₃–SiO₂ mixtures of different mixing ratios during heating.

Fig. 5. Comparison of observed mass loss with the mass losses calculated assuming different reactions being the governing reaction.

The amount of sample mass loss due to CO₂ gas evolution will be determined by the reaction that governs: for example, if the decomposition is governed by the reaction of Eq. (4), each mol of SiO₂ will result in the mass loss equivalent to one mol of CO₂. Similarly, the mass loss for a given mol of SiO₂ by Eqs. (5), (6) and (7) will be equivalent to 0.5, 2 and 4 mols of CO₂, respectively. In the present study the initial sample mass was kept at 50 mg throughout the experiment, and hence different molar ratios of Li₂CO₃/SiO₂ give different total as well as individual number of mols of SiO₂ and Li₂CO₃. The actual number of mols and mass of Li₂CO₃ and SiO₂ in the samples in the different mixing ratios are given in Table 1. In Fig. 5 the mass losses observed up until the time reaches the point indicated by the arrows in Fig. 4 are compared with mass losses calculated assuming different governing reactions (Eqs. (4)–(7)). It is seen that the observed results show good agreement with the results calculated under the assumption that the re-
The action of Eq. (4) governs the process. Therefore the mass balance analysis confirms that \( \text{Li}_2\text{CO}_3 \) and \( \text{SiO}_2 \) initially react with each other to form \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) according to Eq. (4). Once \( \text{Li}_2\text{CO}_3 \) has been exhausted after forming \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \), there is no further reaction taking place (see the results of \( \text{Li}_2\text{CO}_3/\text{SiO}_2 = 1/1, 1/1.5 \) and 1/2 in Fig. 4). On the other hand, if \( \text{SiO}_2 \) has been exhausted and there is a surplus amount of \( \text{Li}_2\text{CO}_3 \) left, further reactions appear to take place as seen in Fig. 4 where for the cases of \( \text{Li}_2\text{CO}_3/\text{SiO}_2 = 1/0.33 \) and 1/0.5 the mass continually decreases after the first decomposition stage according to Eq. (4).

Figure 6 shows the results of X-ray diffraction analysis of some samples after complete decomposition. It is clear that for \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) ratio = 1/1 and 1/1.5 the decomposition product is mostly \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) but for \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) ratio = 1/0.5 the decomposition product is mainly \( 2\text{Li}_2\text{O} \cdot \text{SiO}_2 \). This result indicates that if a surplus of \( \text{Li}_2\text{CO}_3 \) remains after forming \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) according to Eq. (4), the reaction of Eq. (8) begins to take place.

### 3.2. Thermodynamic Predictions

Standard free energy changes of the reactions represented by Eqs. (4) to (9) are plotted against temperature in Fig. 7. It is seen that the initial reaction which is most feasible from thermodynamic point of view is obviously the one represented by Eq. (4). This prediction is in accordance with the observation in that \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) is the only type of silicate found in the experiments as long as both reactants of \( \text{Li}_2\text{CO}_3 \) to \( \text{SiO}_2 \) are available. Strictly speaking, the above free energy analysis is in fact good only when the system is under a thermodynamic equilibrium and all species are in their standard states. The system of the present experimental study, which experiences a rise in temperature at the rate of 10 K min\(^{-1}\) is, however, not necessarily in equilibrium. Nevertheless, the thermodynamic data given in Fig. 7 is found useful in interpreting the reaction mechanism. Careful observation of the mass loss for the cases of surplus \( \text{Li}_2\text{CO}_3 \) (\( \text{Li}_2\text{CO}_3/\text{SiO}_2 = 1/0.33 \) and 1/0.5) in Fig. 4 reveals that upon exhaustion of \( \text{SiO}_2 \) (indicated by arrows) the rate of mass loss becomes quite slow until the temperature reaches around 770°C. It is interesting to notice that the rate in this range is comparable with the one exhibited by \( \text{Li}_2\text{CO}_3 \) decomposition on its own without \( \text{SiO}_2 \) addition (see the curve for \( \text{Li}_2\text{CO}_3/\text{SiO}_2 = 1/0 \) in Fig. 4). The reaction of \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) with the surplus \( \text{Li}_2\text{CO}_3 \) is not thermodynamically feasible to occur up until the temperature reaches about 730°C. Therefore the slow rate of mass loss right after \( \text{SiO}_2 \) exhaustion can be attributed to thermal decomposition of \( \text{Li}_2\text{CO}_3 \) on its own rather than due to reaction of Eq. (8). Once the temperature has reached the point where the reaction of Eq. (8) becomes thermodynamically feasible to occur, the mass loss is then due to both the thermal decomposition of \( \text{Li}_2\text{CO}_3 \) and reaction of Eq. (8). For the case of surplus \( \text{SiO}_2 \) (\( \text{Li}_2\text{CO}_3/\text{SiO}_2 = 1/1.5 \) and 1/2), on the other hand, the reaction between \( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) and surplus \( \text{SiO}_2 \) (Eq. (9)) should be difficult to occur due to thermodynamic driving force being small (Fig. 7) and both reactants (\( \text{Li}_2\text{O} \cdot \text{SiO}_2 \) and \( \text{SiO}_2 \)) being solid. It is then in order to elucidate the actual reaction path that the system of \( \text{Li}_2\text{CO}_3 \) and \( \text{SiO}_2 \) mixture follows.

### 3.3. Reaction Paths

Based on the observations and discussion given above, it is now possible to determine reaction paths that the system comprising \( \text{Li}_2\text{CO}_3 \) and \( \text{SiO}_2 \) follow under the conditions prevailing in the present study. Figure 4 shows that, when a
mixture of Li$_2$CO$_3$ and SiO$_2$ is heated continually, the decomposition of Li$_2$CO$_3$ to an appreciable extent begins to occur at around 600°C. The melting points of Li$_2$CO$_3$ and SiO$_2$ are 733 and 1722°C, respectively. This indicates that the reaction of Eq. (4) to form Li$_2$O·SiO$_2$ begins to take place at a temperature much lower than the melting point of either reactant. The reaction product of Li$_2$O·SiO$_2$ melts congruently at 1201°C as can be seen in Fig. 8. The reaction of Eq. (4), therefore, appears to involve the reactants and product being all solid phases except CO$_2$ gas. A reaction between all solid reactants which produces a solid product is not kinetically feasible enough to proceed at any reasonable rate due to limited contact points and self-blocking by the product. It is therefore reasonable to suspect that the Li$_2$CO$_3$–SiO$_2$ system might form a liquid phase in a particular compositional range. Since Li$_2$CO$_3$ and Li$_2$O exhibit mutual liquid solubility at elevated temperatures, the system on hand can be considered to be a Li$_2$CO$_3$–Li$_2$O–SiO$_2$ ternary system. The phase relationship of this ternary system is not available. However, it is possible to make a rough estimate of the ternary relationship by employing a computational thermodynamic technique based on thermodynamic information available on binary systems. The results are given in Fig. 9. It is seen that it predicts that the ternary system exhibits a liquidus temperature below 600°C in a particular compositional range. This implies that the major reaction between Li$_2$CO$_3$ and SiO$_2$ is not a solid–solid reaction, but a reaction in the liquid solution consisting of Li$_2$CO$_3$–SiO$_2$–Li$_2$O–Li$_2$CO$_3$ ternary system estimated using thermodynamic information available in the literature.®

Fig. 8. Equilibrium phase diagram of the Li$_2$O–SiO$_2$ binary system.

Fig. 9. SiO$_2$–Li$_2$O–Li$_2$CO$_3$ ternary phase diagram estimated using thermodynamic information available in the literature.®
Li₂CO₃, Li₂O and SiO₂. Assuming that the above ternary phase prediction is reasonably acceptable, the reaction of Eq. (4) may be rewritten as follows:

\[
\text{(Li}_2\text{CO}_3) + \text{(SiO}_2\text{)} = \text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2(g) \quad (10)
\]

where species in the round brackets indicate the ones in the liquid solution.

In order to identify the formation of liquid phase a sample was quenched in the middle of the decomposition process, and the result is given in Fig. 10, which also includes the starting materials. It is clear from the figure that a liquid layer does in fact form in the vicinity of a SiO₂ particle, in which the concentration gradient of SiO₂ is clearly identified.

From the prediction of phase equilibrium and experimental results mentioned above, the chemical interaction of Li₂CO₃ and SiO₂ can be considered to proceed in the following manner:

(a) Initially a solid–solid reaction between Li₂CO₃(s) and SiO₂(s) occurs to form Li₂O·SiO₂:

\[
\text{Li}_2\text{CO}_3(s) + \text{SiO}_2(s) \rightarrow \text{Li}_2\text{O} \cdot \text{SiO}_2(s) + \text{CO}_2(g) \quad (4)
\]

(b) A layer of a liquid solution consisting of Li₂CO₃, SiO₂ and Li₂O forms between Li₂CO₃(s) and SiO₂(s) particles by mutual dissolution of Li₂CO₃(s), SiO₂(s) and Li₂O·SiO₂(s) at temperatures below 600°C (see Fig. 9).

(c) Li₂CO₃(s) and SiO₂(s) continues to dissolve into the liquid layer. The composition of the liquid solution will be influenced by the relative dissolution rate of these species as follows:

\[
\text{Li}_2\text{CO}_3(s) \rightarrow (\text{Li}_2\text{CO}_3) \quad (11)
\]

SiO₂(s)→(SiO₂) .............................................(12)

(d) Chemical reactions taking place in the solution include the following:

\[
\text{(Li}_2\text{CO}_3) + \text{(SiO}_2\text{)} = \text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2(g) \quad (13)
\]

\[
\text{(Li}_2\text{CO}_3) + \text{(SiO}_2\text{)} = \text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2 + \text{CO}_2(g) \quad (14)
\]

The mass loss in the present system is solely due to CO₂ gas evolution. From Figs. 4 and 5 it is clear that the reaction of Eq. (14) is responsible for the mass loss. If the reaction of Eq. (13) were the governing one, the initial mass loss would be independent of Li₂O·SiO₂ formation and hence unable to account for the mass loss behavior shown in Fig. 5.

(e) The reaction of Eq. (14) continues to occur until either Li₂CO₃ or SiO₂ has been exhausted. For the case where SiO₂ is exhausted first (Li₂CO₃/SiO₂=1/0.33 and 1/0.5 in the present study), further mass loss is due to both the thermal decomposition of the excess Li₂CO₃ and the reaction between the Li₂CO₃ and the Li₂O·SiO₂ product. However, the latter reaction does not occur until the temperature reaches the point at which the reaction becomes thermodynamically feasible (about 770°C in the present study), and hence the slow rate right after SiO₂ exhaustion is mainly due to the thermal decomposition of Li₂CO₃. The reaction product after completion at 1000°C has been identified to be 2Li₂O·SiO₂ (Fig. 6). Therefore, after exhaustion of SiO₂ the following reactions take place:

\[
\text{(Li}_2\text{CO}_3) = \text{(Li}_2\text{O}) + \text{CO}_2(g) \quad (15)
\]

\[
\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{(Li}_2\text{O}) = 2\text{Li}_2\text{O} \cdot \text{SiO}_2 \quad (16)
\]

\[
\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{(Li}_2\text{CO}_3) = 2\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{CO}_2(g) \quad (17)
\]

(f) On the other hand, for the case where Li₂CO₃ is exhausted first (Li₂CO₃/SiO₂=1/1.5 and 1/2 in the present study), it might be possible to form Li₂O·2SiO₂ by further reaction between the excess SiO₂ and the product Li₂O·SiO₂:

\[
\text{Li}_2\text{O} \cdot \text{SiO}_2 + \text{SiO}_2 = \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \quad (9)
\]

However, the experimental results prove that this is not the case (Fig. 4). The XRD analysis reveals that no further reaction proceeds between Li₂O·SiO₂ and SiO₂ (Fig. 6). This may be attributed to the fact that once Li₂CO₃ has been exhausted, there is no liquid solution left (Figs. 8 and 9), and hence any further reaction should be a solid–solid reaction which is unlikely to proceed at any appreciable rate. Furthermore, thermodynamic driving force for the reaction is low (Fig. 7).

The rate of the reaction process in the above will be enhanced over time, since the temperature rises with time. This is seen clearly in Figs. 3 and 4. For the case of the 1/1 Li₂CO₃/SiO₂ mixing ratio which is the exact stoichiometric ratio for the reaction of Eq. (14), the decomposition product should be Li₂O·SiO₂ only. As seen in Fig. 6, the majority of the product is indeed Li₂O·SiO₂. However, some amount of SiO₂ and 2Li₂O·SiO₂ are also identified. This can be explained in conjunction with the decomposition curve for the 1/1 Li₂CO₃/SiO₂ ratio in Fig. 4. In this...
case, as the decomposition approaches completion, the amount of LiO$_2$·SiO$_2$, which is solid, increases at the expense of the liquid phase and hence the transfer of Li$_2$O, Li$_2$CO$_3$, and SiO$_2$ in the liquid phase is hindered. This is attributed to the rate of decomposition being sluggish toward completion of the decomposition (Fig. 4) and the small residual amounts of SiO$_2$ and 2Li$_2$O·SiO$_2$ due to further local reactions between Li$_2$O·SiO$_2$ and SiO$_2$ (Fig. 6).

3.4. Activation Energy of Decomposition

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

$$\frac{dX}{dt} = kX^n$$ ..................................(18)

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

$$k = Ae^{-E/R}$$ ..................................(19)

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. (18) and (19), Freeman–Carroll derived the following equation:

$$-\frac{E}{2.3R} \log \left(\frac{1}{T} \right) = -n + \frac{\Delta \log W_r}{\Delta \log W_t}$$ ..................................(20)

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

By plotting Eq. (20), the order of reaction and the activation energy for the reaction can be obtained. A plot of Eq. (20) for the decomposition of Li$_2$CO$_3$ with SiO$_2$ given in Fig. 4 is shown in Fig. 11. The plot shows a reasonably good linear relationship. The activation energy of the decomposition reaction of Li$_2$CO$_3$ with SiO$_2$ is found to be 198 kJ mol$^{-1}$. The relatively high activation energy of Li$_2$CO$_3$ decomposition with SiO$_2$ implies that the rate controlling step of the decomposition of Li$_2$CO$_3$ with SiO$_2$ should be the one with the rate greatly enhanced by thermal energy. Therefore this, together with the fact that the liquid phase is stirred by the CO$_2$ gas generated by the decomposition reaction, which in turn enhances the liquid phase mass transfer, leads to the conclusion that the reaction of Eq. (14) is the rate controlling step.

4. Conclusions

The effect of SiO$_2$ addition on the decomposition of Li$_2$CO$_3$ was investigated using the thermo-gravimetric and differential scanning calorimetric method (TG-DSC) at temperatures up to 1000°C. The findings are summarized in the following:

1) The decomposition of Li$_2$CO$_3$ is greatly enhanced when mixed with SiO$_2$. The decomposition rate of Li$_2$CO$_3$ with SiO$_2$ was much greater than that with carbon.

2) The primary decomposition reaction begins to take place at around 600°C, a much lower temperature than the melting point of either Li$_2$CO$_3$ (733°C) or SiO$_2$ (1722°C).

3) The decomposition product is Li$_2$O·SiO$_2$ irrespective of the mixing ratio of Li$_2$CO$_3$ to SiO$_2$ until either one of the reactants has been exhausted.

4) The decomposition rate is independent of the Li$_2$CO$_3$/SiO$_2$ mixing ratio until either one has completely been consumed.

5) The decomposition mechanism of Li$_2$CO$_3$ with SiO$_2$ are described as follows:

- A liquid layer of the solution of Li$_2$CO$_3$, Li$_2$O and SiO$_2$ forms between Li$_2$CO$_3$(s) and SiO$_2$(s) particles at temperatures lower than 600°C.
- While Li$_2$CO$_3$(s) and SiO$_2$(s) continue to dissolve into the liquid layer, Li$_2$O·SiO$_2$ forms until either reactant has fully consumed:

$$\text{Li}_2\text{CO}_3(s) + \text{SiO}_2(s) \rightarrow \text{Li}_2\text{O·SiO}_2(s)$$

- When SiO$_2$ is exhausted, the reaction product of Li$_2$O·SiO$_2$ undergoes a further reaction with the excess Li$_2$CO$_3$:

$$\text{Li}_2\text{CO}_3(s) + \text{SiO}_2(s) \rightarrow 2\text{Li}_2\text{O·SiO}_2(s)$$

- When Li$_2$CO$_3$ is exhausted first, on the other hand, no further reaction between Li$_2$O·SiO$_2$ and the excess SiO$_2$ takes place.

- The apparent activation energy of the Li$_2$CO$_3$ decomposition in existence with SiO$_2$ is 198 kJ mol$^{-1}$.

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