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Decomposition of Li_2CO_3 in existence of SiO_2 in mould flux of steel casting

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The effect of SiO_2 addition on the decomposition of Li_2CO_3 was investigated at temperatures up to 1000ºC. It was found that addition of SiO_2 greatly enhanced the decomposition of Li_2CO_3. The main decomposition reaction started at around 600ºC, and completed just above the melting point of Li_2CO_3. The major decomposition product was $Li_2O•SiO_2$ irrespective of the Li_2CO_3 to SiO_2 mixing ratio while both reactants were available. It was ascertained that a liquid layer between Li_2CO_3 and SiO_2 particles formed and facilitated the decomposition reaction. The governing reaction of the decomposition was the one between the dissolved Li_2CO_3 and SiO_2 in the liquid layer to form $Li_2O•SiO_2$. The decomposition rate was independent of the Li_2CO_3/SiO_2 mixing ratio until either one had been completely exhausted. When excess Li_2CO_3 existed, it further reacted with the initial product of $Li_2O•SiO_2$ to form $2Li_2O•SiO_2$. 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_2CO_3 exhaustion there is no liquid phase available to facilitate further reaction. The apparent activation energy of the decomposition of Li_2CO_3 in existence with SiO_2 is 198 kJ mol^{-1}.

Introduction

Li_2O is a commonly used additive to mould flux and is generally added at 1 to 20 wt.%[1] to control the melting behaviour and fluidity of the mould flux. In most cases, Li_2O is added in the form of Li_2CO_3, which is subjected to decomposition at an elevated temperature in the casting mould. It was reported recently that the increase in melting rate of the mould flux by addition of carbonates such as Na_2CO_3 and Li_2CO_3 is due to the increase in thermal conductivity of the mould flux by gases generated during decomposition of these carbonates.[2] If the amount of carbonates is excessive, it has been reported that turbulence in the mould is caused due to intense evolution of gases. In order to maximize the beneficial effects of carbonates addition, therefore, it is essential to understand in detail how they interact with other components in the mould flux and hence influence the melting behaviour of the mould flux. Recently the authors reported their study on the decomposition of Na_2CO_3 on its own, with carbon and SiO_2, and decomposition of Li_2CO_3 on its own and with carbon.[3]

In the present study, it was attempted to elucidate the decomposition behaviour of Li_2CO_3 by interaction with SiO_2.

Table I
Chemical composition of the materials (mass %)

	Li_2CO_3	SiO_2	Carbon black
SiO_2	-	96.3	-
Li_2O	38.8	-	-
Total C	16	0.3	99.9
CO_2	58.6	-	-

Experimental

Table I gives the chemical composition of the materials used in the present study. A thermal analyzer equipped with both thermo-gravimetric (TG) and differential scanning calorimetric (DSC) functions was employed in the present experimental study. It enabled simultaneous analysis of TG and DSC with a detection accuracy of ±1μg. Inert atmosphere was maintained during the experiment by flowing purified argon gas at the rate of 5 x 10^{-5} m^3min^{-1}. The sample mass for each run was in the range of 15 to 50 mg depending on experimental conditions. Several different Li_2CO_3 to SiO_2 mixing ratios were employed to determine how the ratio affects the decomposition behaviour.

Decomposition of pure Li_2CO_3 and Li_2CO_3 mixed with carbon was also investigated for the purpose of comparison. Al_2O_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 10ºC min^{-1}. 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.

Results and discussion

Observations

Figure 1 shows a typical TG-DSC result of the decomposition of Li_2CO_3 mixed together with SiO_2. The decomposition behaviour of pure Li_2CO_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

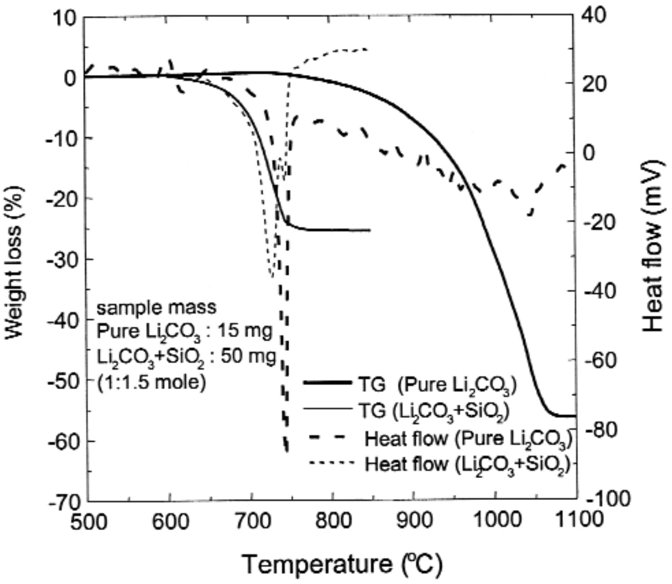

Figure 1. TG-DSC results with pure Li_2O_3 and mixture of Li_2CO_3 and SiO_2 (heating rate: 10ºC min^{-1})

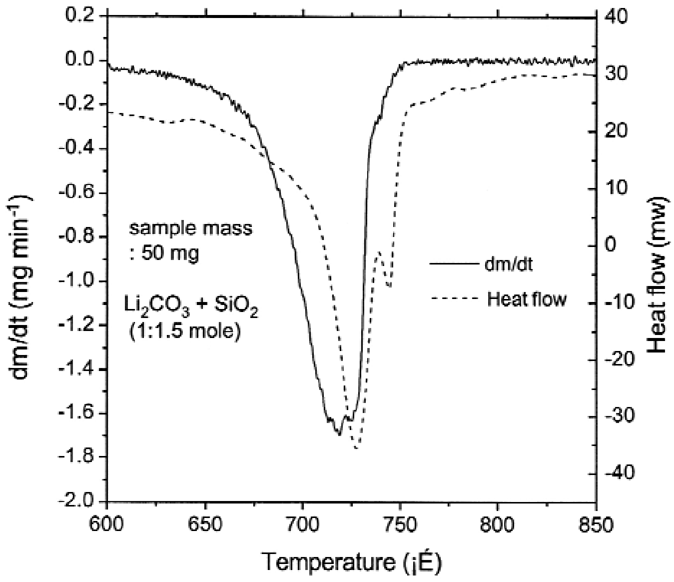

Figure 2. Changes in the rate of mass loss and heat flow during TG-DSC analysis of Li_2CO_3 mixed with SiO_2 (heating rate: 10ºC min^{-1})

when it is subjected to continuous heating (10ºC per minute). It is clear from the figure that the decomposition behaviour of Li_2CO_3 is vastly different between the two cases. Li_2CO_3 begins to decompose at around 600ºC when mixed with SiO_2, whereas pure Li_2CO_3 hardly decomposes at this temperature, and the decomposition rate is quite slow even after melting (see the endothermic peak in Figure 1). Moreover, the Li_2CO_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_2CO_3 mixed with SiO_2 in the Li_2CO_3/SiO_2 ratio = 1/1.5. The rate reaches its maximum when the temperature approaches the melting point of Li_2CO_3. Figures 1 and 2 also show that the decomposition of Li_2CO_3 is complete just after the temperature has reached the melting point of Li_2CO_3 (733ºC).4) It is now obvious that existence of SiO_2 greatly enhances the decomposition of Li_2CO_3. Reactions that are responsible for the decomposition of Li_2CO_3 in a usual mould flux system include:

$$Li_2CO_3 = Li_2O + CO_2(g) \quad [1]$$

$$Li_2CO_3 + C = Li_2O + 2CO(g) \quad [2]$$

$$xLi_2CO_3 + ySiO_2 = (xLi_2O - ySiO_2) + xCO_2(g) \quad [3]$$

In order to examine which of the above reactions would dominate the decomposition of Li_2CO_3 in a mould flux system that contains both carbon and SiO_2, a separate experiment was carried out with a mixture of Li_2CO_3 and carbon black, and results are given in Figure 3. It is clear that the decomposition of Li_2CO_3 mixed with SiO_2 occurs at a much lower temperature and is nearly complete by the time the decomposition of Li_2CO_3 mixed with carbon black is just begining to take place. The above observations confirm the view that decomposition of Li_2CO_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_2CO_3 decomposition, experiments were carried out with samples prepared with a number of different Li_2CO_3 to SiO_2 mixing ratios of, i.e., Li_2CO_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 Figure 4. It is seen that, except in the case of non-addition of SiO_2, 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 Li_2CO_3 in coexistence with SiO_2 is governed by an identical reaction mechanism, irrespective of the relative amount of SiO_2 until the time indicated by the arrow is reached. Considering compounds to be formed in the Li_2CO_3-SiO_2- system, the reaction represented by Equation [3] may be rewritten as follows:

$$Li_2CO_3 + SiO_2 = Li_2O \cdot SiO_2 + CO_2(g) \quad [4]$$

$$1/2Li_2CO_3 + SiO_2 = 1/2Li_2O \cdot 2SiO_2 + 1/2CO_2(g) \quad [5]$$

$$2Li_2CO_3 + SiO_2 = 2Li_2O \cdot SiO_2 + 2CO_2(g) \quad [6]$$

$$4Li_2CO_3 + SiO_2 = 4Li_2O \cdot SiO_2 + 4CO_2(g) \quad [7]$$

$$Li_2O \cdot SiO_2 + Li_2CO_3 = 2Li_2O \cdot SiO_2 + CO_2 \quad [8]$$

$$Li_2O \cdot SiO_2 + SiO_2 = Li_2O \cdot SiO_2 \quad [9]$$

The amount of sample mass loss due to CO_2 gas evolution will be determined by the reaction that governs: for example, if the decomposition is governed by the reaction of Equation [4], each mol of SiO_2 will result in the mass loss equivalent to one mol of CO_2. Similarly, the mass loss for a given mol of SiO_2 by Equations [5], [6] and [7] will be equivalent to 0.5, 2 and 4 mols of CO_2, respectively.

In the present study the initial sample mass was kept at 50 mg throughout the experiment, and hence different molar ratios of Li_2CO_3/SiO_2 give different totals as well as individual numbers of moles of SiO_2 and Li_2CO_3. The actual number of mols and mass of Li_2CO_3 and SiO_2 in the samples in the different mixing ratios are given in Table II.

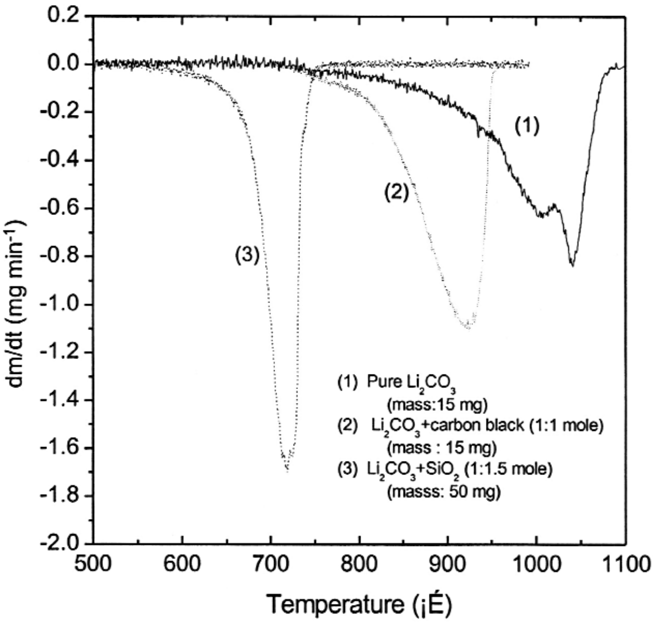

Figure 3. Changes in the rate of mass loss due to decomposition of Li_2CO_3: (1) pure Li_2CO_3, (2) Li_2CO_3 with carbon black, (3) Li_2CO_3 with SiO_2 (heating rate: 10°C min^{-1})

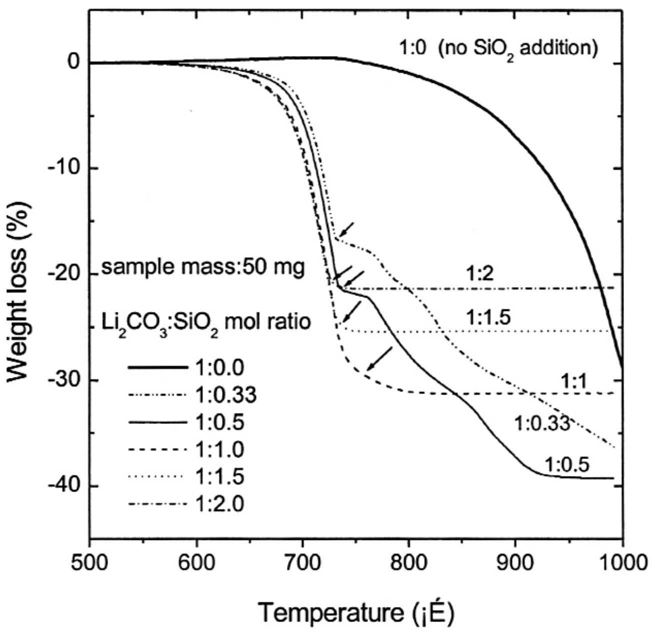

Figure 4. Mass loss of Li_2CO_3-SiO_2 mixtures of different mixing ratios during heating (heating rate: 10°C min^{-1}) note that except in the case of no SiO_2 addition, the mass loss with time (or temperature) for each mixing ratio follows a nearly identical path until the time reaches the point indicated by an arrow

In Figure 5 the mass losses observed up until the time reaches the point indicated by the arrows in Figure 4 are compared with mass losses calculated assuming different governing reactions (Equations [4]–[7]). It is seen that the observed results show good agreement with the results calculated under the assumption that the reaction of Equation [4] governs the process.

Therefore the mass balance analysis confirms that Li_2CO_3 and SiO_2 initially react with each other to form $Li_2O{\bullet}SiO_2$ according to Equation [4]. Once Li_2CO_3 has been exhausted after forming $Li_2O{\bullet}SiO_2$, no further reaction takes place (see the results of Li_2CO_3/SiO_2 = 1/1, 1/1.5 and 1/2 in Figure 4). On the other hand, if SiO_2 has been exhausted and there is a surplus amount of Li_2CO_3 left, further reactions appears to take place, as seen in Figure 4 where for the cases of Li_2CO_3/SiO_2 = 1/0.33 and 1/0.5 the mass continually decreases after the first decomposition stage according to Equation [4].

Figure 6 shows the results of X-ray diffraction analysis of some samples after complete decomposition. It is clear that for Li_2CO_3/SiO_2 ratio = 1/1 and 1/1.5 the decomposition product is mostly $Li_2O{\bullet}SiO_2$ but for Li_2CO_3/SiO_2 ratio = 1/0.5 the decomposition product is mainly $2Li_2O{\bullet}SiO_2$. This result indicates that if a surplus of Li_2CO_3 remains after forming $Li_2O{\bullet}SiO_2$ according to Equation [4], the reaction of Equation [8] begins to take place.

Table II
Mass and mol of Li_2CO_3 and SiO_2 in samples of different Li_2CO_3 (the total sample mass was kept constant at 50mg)

Li_2CO_3/	mg		mo1	
SiO_2	Li_2CO_3	SiO_2	LIi_2CO_3	SiO_2
1.0/0.33	39.45	10.55	0.533	0.177
1.0/0.5	35.58	14.42	0.482	0.242
1.0/1.0	27.61	22.39	0.373	0.373
1.0/1.0	22.57	27.43	0.305	0.458
1.0/2.0	19.02	30.98	0.258	0.515

Thermodynamic predictions and reaction paths

Standard free energy changes of the reactions represented by Equations [4] to [9] are plotted against temperature in Figure 7.[5] It is seen that the initial reaction, which is most feasible from thermodynamic point of view, is obviously the one represented by Equation [4]. This prediction is in accordance with the observation that $Li_2O{\bullet}SiO_2$ is the only type of silicate found in the experiments as long as both reactants of Li_2CO_3 to 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 Figure 7 is found useful in interpreting the reaction mechanism. Careful observation of the mass loss for the cases of surplus Li_2CO_3 (Li_2CO_3/SiO_2 = 1/0.33 and 1/0.5) in Figure 4 reveals that, upon exhaustion of SiO_2 (indicated by arrows), the rate of mass loss becomes quite slow until the temperature reaches around 770°C. It is interesting to note that the rate in this range is comparable with the one exhibited by Li_2CO_3 decomposition on its own without SiO_2 addition (See the curve for Li_2CO_3/SiO_2 = 1/0 in Figure 4). It is not thermodynamically feasible for the reaction of $Li_2O{\bullet}SiO_2$ with the surplus Li_2CO_3 to occur up until the temperature reaches about 730°C. Therefore the slow rate of mass loss right after SiO_2 exhaustion can be attributed to thermal decomposition of Li_2CO_3 on its own rather than due to reaction of Equation [8]. Once the temperature has reached the point where the reaction of Equation [8] becomes thermodynamically feasible, the mass loss is then due to

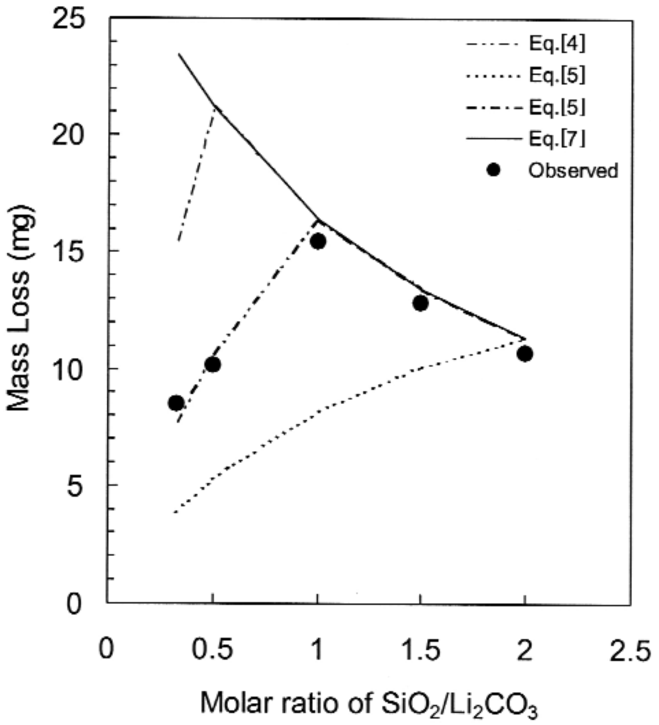

Figure 5. Comparison of observed mass loss with the mass losses calculated assuming different reactions being the governing reaction

both the thermal decomposition of Li_2CO_3 and reaction of Equation [8]. For the case of surplus SiO_2 (Li_2CO_3/SiO_2 = 1/1.5 and 1/2), on the other hand, the reaction between $Li_2O{\bullet}SiO_2$ and surplus SiO_2 (Equation [9]) should be difficult due to the thermodynamic driving force being small (Figure 7) and both reactants ($Li_2O{\bullet}SiO_2$ and SiO_2) being solid. It is then in order to elucidate the actual reaction path that the system of Li_2CO_3 and SiO_2 mixture follows.

Based on the observations and discussion given above, it is now possible to determine reaction paths that the system comprising Li_2CO_3 and SiO_2 follow under the conditions prevailing in the present study. Figure 4 shows that, when a mixture of Li_2CO_3 and SiO_2 is heated continually, the decomposition of Li_2CO_3 to an appreciable extent begins to occur at around 600ºC. The melting points of Li_2CO_3 and SiO_2 are 733ºC and 1722ºC, respectively.[4] This indicates that the reaction of Equation [4] to form $Li_2O{\bullet}SiO_2$ begins to take place at a temperature much lower than the melting point of either reactant. The reaction product of $Li_2O{\bullet}SiO_2$ melts congruently at 1201ºC as can be seen in Figure 8.[6]

The reaction of Equation [4], therefore, appears to involve the reactants and product being all solid phases except CO_2 gas. A reaction between all solid reactants that 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_2CO_3-SiO_2 system might form a liquid phase in a particular compositional range. Since Li_2CO_3 and Li_2O exhibit mutual liquid solubility at elevated temperatures, the system on hand can be considered to be a Li_2CO_3-Li_2O-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 Figure 9.[7] It is seen that it predicts that the ternary system exhibits a liquidus temperature below 600ºC in a particular compositional range. This implies that the major reaction between Li_2CO_3 and SiO_2 is not a solid-solid reaction, but a reaction in the liquid solution consisting of Li_2CO_3, Li_2O and SiO_2. Assuming that the above ternary phase prediction is reasonably acceptable, the reaction of Equation [4] may be rewritten as follows:

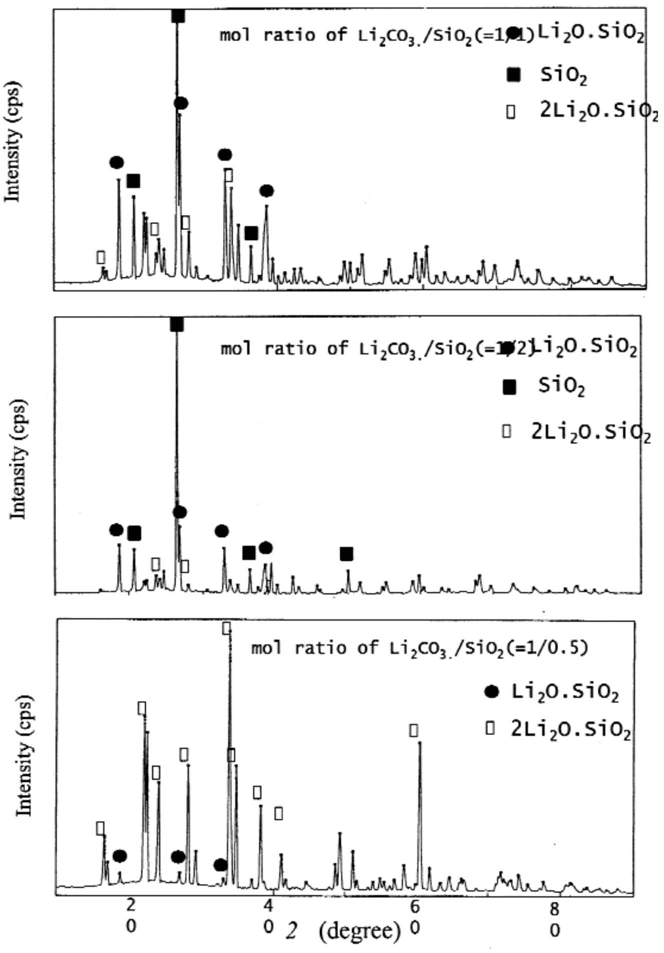

Figure 6. Results of X-ray diffraction analysis of products formed by decomposition of Li_2CO_3 mixed with SiO_2

$$(Li_2CO_3)+(SiO_2)=Li_2O\cdot SiO_2+CO_2(g) \qquad [10]$$

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 Figure 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 SiO_2 particle, in which the concentrational gradient of SiO_2 is clearly identified.

From the prediction of phase equilibrium and experimental results mentioned above, the chemical interaction of Li_2CO_3 and SiO_2 can be considered to proceed in the following manner:

(a) Initially a solid-solid reaction between Li_2CO_3(s) and SiO_2(s) occurs to form $Li_2O{\bullet}SiO_2$ (Equation [4])
(b) A layer of a liquid solution consisting of Li_2CO_3,

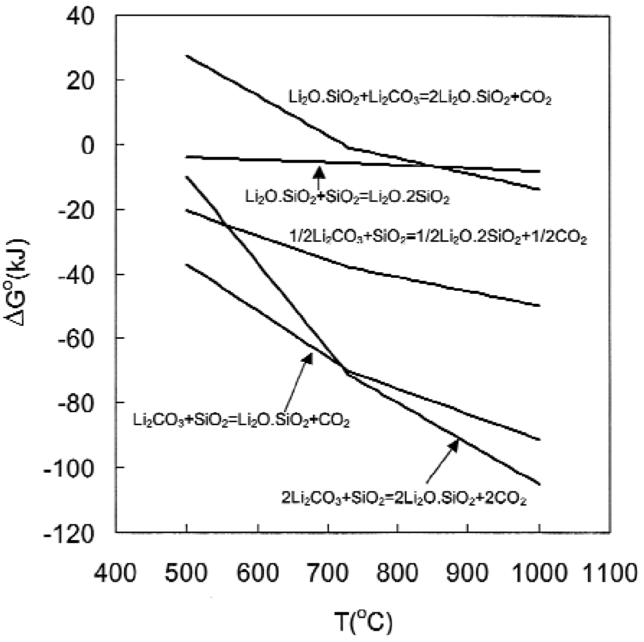

Figure 7. Standard free energy changes of various reactions in the system comprising Li_2CO_3 and SiO_2

SiO_2 and Li_2O forms between Li_2CO_3(s) and SiO_2(s) particles by mutual dissolution of Li_2CO_3(s), SiO_2(s) and $Li_2O•SiO_2$(s) below 600°C.

(c) Li_2CO_3(s) and SiO_2(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.

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

$$(Li_2CO_3) \rightarrow (Li_2O) + CO_2 \qquad [11]$$

$$(Li_2CO_3) + (SiO_2) \rightarrow Li_2O \cdot SiO_2 + CO_2 \qquad [12]$$

The mass loss in the present system is solely due to CO_2 gas evolution. From Figures 4 and 5 it is clear that the reaction of Equation [12] is responsible for the mass loss. If the reaction of Equation [11] were the governing one, the initial mass loss would be independent of $Li_2O•SiO_2$ formation and hence unable to account for the mass loss behaviour shown in Figure 5.

(e) The reaction of Equation [12] continues to occur until either Li_2CO_3 or SiO_2 has been exhausted. For the case where SiO_2 is exhausted first (Li_2CO_3/SiO_2 = 1/0.33 and 1/0.5 in the present study), further mass loss is due to both the thermal decomposition of the excess Li_2CO_3 and the reaction between the Li_2CO_3 and the $Li_2O•SiO_2$ 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 SiO_2 exhaustion is mainly due to the thermal decomposition of Li_2CO_3. The reaction product after completion at 1000°C has been identified to be $2Li_2O•SiO_2$ (Figure 6). Therefore, after exhaustion of SiO_2 the following reactions take place:

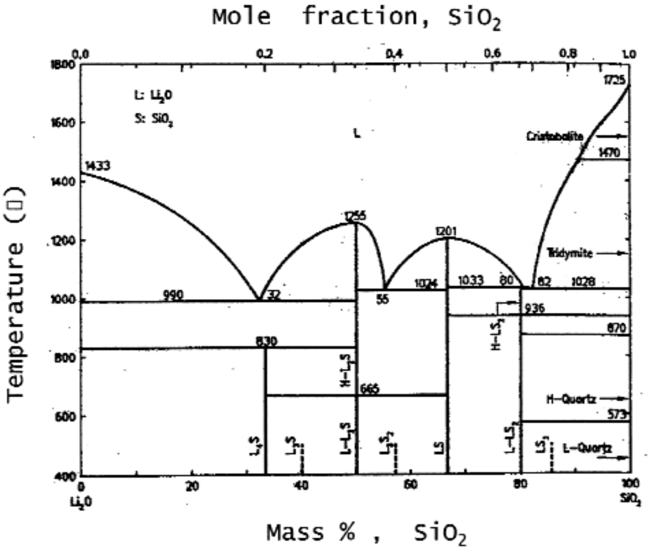

Figure 8. Equilibrium phase diagram of the Li_2O-SiO_2 binary system

$$(Li_2CO_3) = (Li_2O) + CO_2(g) \qquad [13]$$

$$Li_2O \cdot SiO_2 + (Li_2O) = 2Li_2O \cdot SiO_2 \qquad [14]$$

$$Li_2O \cdot SiO_2 + (Li_2CO_3) = 2Li_2O \cdot SiO_2 + CO_2(g) \qquad [15]$$

(f) On the other hand, for the case where Li_2CO_3 is exhausted first (Li_2CO_3/SiO_2 = 1/1.5 and 1/2 in the present study), it might be possible to form $Li_2O•2SiO_2$ by further reaction between the excess SiO_2 and the product $Li_2O•SiO_2$ (Equation [9]). However, the experimental results prove that this is not the case (Figure 4). The XRD analysis reveals that no further reaction proceeds between $Li_2O•SiO_2$ and SiO_2 (Figure 6). This may be attributed to the fact that once Li_2CO_3 has been exhausted, there is no liquid solution left (Figures 8 and 9), and hence any further reaction should be a solid-solid reaction which is unlikely to proceed at any appreciable rate. Furthermore, the thermodynamic driving force for the reaction is low (Figure 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 Figures 3 and 4. For the case of the 1/1 Li_2CO_3/SiO_2 mixing ratio, which is the exact stoichiometric ratio for the reaction of Equation [14], the decomposition product should be $Li_2O•SiO_2$ only. As seen in Figure 6, the majority of the product is indeed $Li_2O•SiO_2$. However, some amounts of SiO_2 and $2Li_2O•SiO_2$ are also identified. This can be explained in conjunction with the decomposition curve for the 1/1 Li_2CO_3/SiO_2 ratio in Figure 4. In this case, as the decomposition approaches completion, the amount of $Li_2O•SiO_2$, which is solid, increases at the expense of the liquid phase and hence the transfer of Li_2O, Li_2CO_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 (Figure 4) and the small residual amounts of SiO_2 and $2Li_2O•SiO_2$ due to further local reactions between $Li_2O•SiO_2$ and SiO_2 (Figure 6).

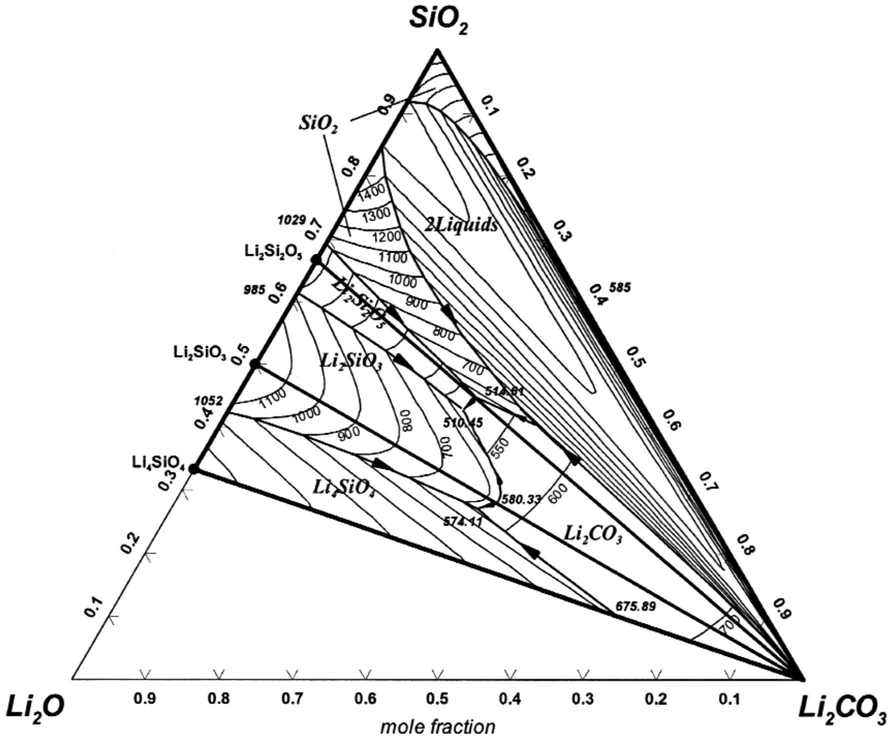

Figure 9. SiO_2-Li_2O-Li_2CO_3 ternary phase diagram estimated using thermodynamic information available in the literature[5,6]

Activation energy of decomposition

The Freeman-Carroll method[8] 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

$$-\frac{dX}{dt} = kX^n \qquad [18]$$

where, X is the amount of the reactant at time t, k is the specific rate constant,and 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

$$k = Ae^{-E/RT} \qquad [19]$$

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

From Equations [18] and [19], Freeman-Carroll derived the following equation:

$$-\frac{\frac{E}{2.3R}\Delta\left(\frac{1}{T}\right)}{\Delta\log W_r} = -n + \frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log W_r} \qquad [20]$$

$$W_r = w_c - w \qquad [21]$$

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

By plotting Equation [20], the order of reaction and the activation energy for the reaction can be obtained. A plot of Equation [20] for the decomposition of Li_2CO_3 with SiO_2 given in Figure 4 is shown in Figure 11. The plot shows a

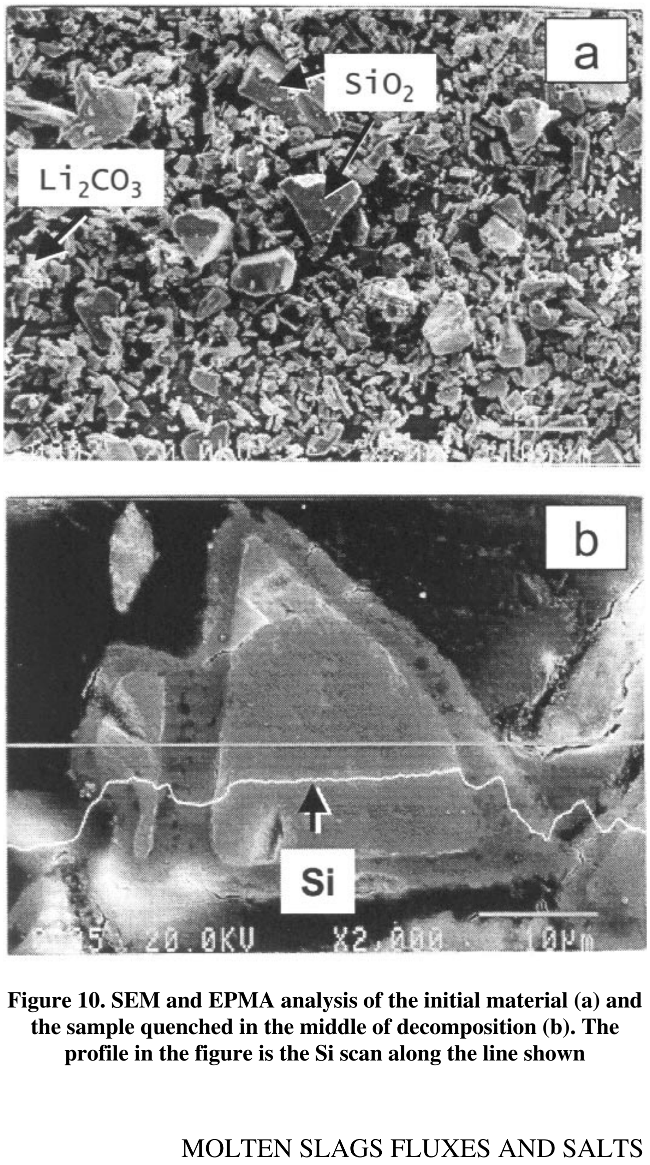

Figure 10. SEM and EPMA analysis of the initial material (a) and the sample quenched in the middle of decomposition (b). The profile in the figure is the Si scan along the line shown

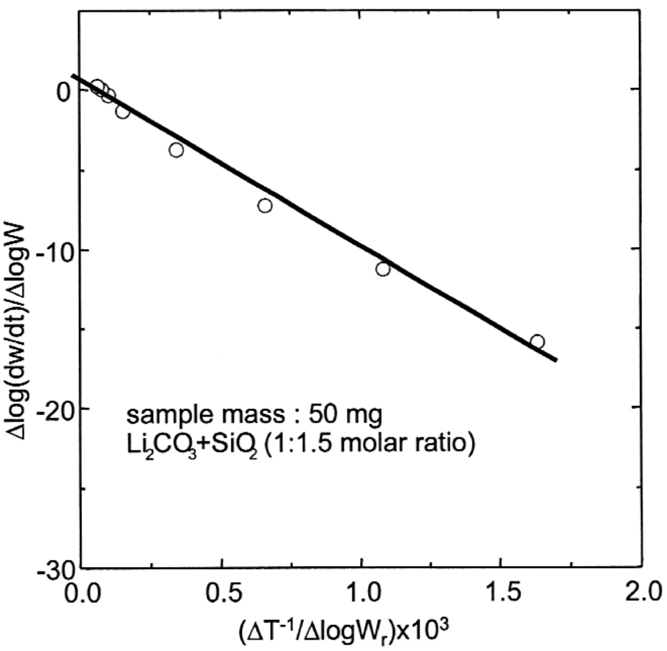

Figure 11. Kinetics of thermal decomposition of Li_2CO_3 with SiO_2

reasonably good linear relationship. The activation energy of the decomposition reaction of Li_2CO_3 with SiO_2 is found to be 198 kJ mol^{-1}. The relatively high activation energy of Li_2CO_3 decomposition with SiO_2 implies that the rate controlling step of the decomposition of Li_2CO_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 Equation [14] is the rate controlling step.

Conclusions

The effect of SiO_2 addition on the decomposition of Li_2CO_3 was investigated using the thermo-gravimetric and differential scanning calorimetric method (TG-DSC) at temperatures up to 1000°. The findings are summarized as follows:

- The decomposition of Li_2CO_3 is greatly enhanced when mixed with SiO_2. The decomposition rate of Li_2CO_3 with SiO_2 was much greater than that with carbon.
- The primary decomposition reaction begins to take place at around 600°C, a much lower temperature than the melting point of either Li_2CO_3 (733°C) or SiO_2 (1722°).
- The decomposition product is $Li_2O \bullet SiO_2$ irrespective of the mixing ratio of Li_2CO_3 to SiO_2 until either one of the reactants has been exhausted.
- The decomposition rate is independent of the Li_2CO_3/SiO_2 mixing ratio until either one has been completely consumed.
- The decomposition mechanism of Li_2CO_3 with SiO_2 are described as follows:
  - A liquid layer of the solution of Li_2CO_3, Li_2O and SiO_2 forms between $Li_2CO_3(s)$ and $SiO_2(s)$ particles at temperatures lower than 600°C.
  - While $Li_2CO_3(s)$ and $SiO_2(s)$ continue to dissolve into the liquid layer, $Li_2O \bullet SiO_2$ forms until either reactant has been fully consumed.
  - When SiO_2 is exhausted, the reaction product of $Li_2O \bullet SiO_2$ undergoes a further reaction with the excess Li_2CO_3 to form $2Li_2O \bullet SiO_2$.
  - When Li_2CO_3 is exhausted first, on the other hand, no further reaction between $Li_2O \bullet SiO_2$ and the excess SiO_2 takes place.
- The apparent activation energy of the Li_2CO_3 decomposition in existence with SiO_2 is 198 kJ mol^{-1}.

Acknowledgments

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