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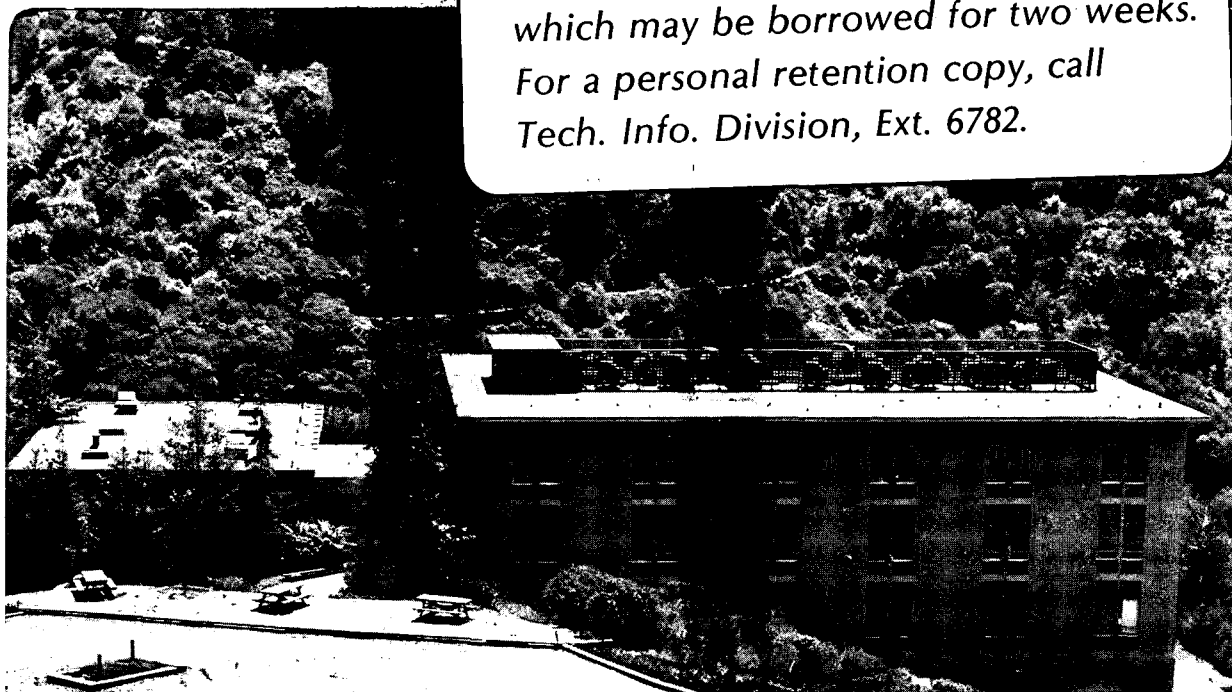
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The Effect of Lithium Carbonate on the Reaction
of CaO Powders with CO₂

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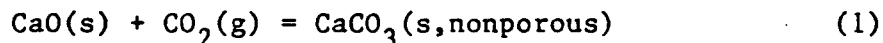
Abstract

Reaction between CaO powders and CO₂(g) is often limited by slow diffusion of CO₂ through the CaCO₃ product. Additions of Li₂CO₃ are shown to increase the reaction rate. At temperatures near or higher than the Li₂CO₃-CaCO₃ eutectic temperature, 935 K, complete reaction of the CaO can be achieved when the heating rate and Li₂CO₃ content are optimized. At lower temperatures Li₂CO₃ causes less but measurable increases in reaction rates. SEM and surface area observations suggest different reaction paths when Li₂CO₃ is present, when Li₂CO₃ and eutectic are present, and when eutectic alone is present.

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INTRODUCTION

Reactions between a solid reagent and a gaseous phase to form a nonporous solid product are often limited by a slow step controlled by the diffusion of the gaseous phase through the newly formed polycrystalline phase. For the reaction:



Barker [1] found that CaO samples with a large number of very small pores (<4 nm) react with CO₂ initially very quickly, and then at a much slower rate due to the diffusion of the gaseous phase through the nonporous CaCO₃ layer. The critical CaCO₃ layer thickness where this change takes place was 22 nm. Oakeson and Cuttler [2], working with CaO nonporous samples, studied the same reaction as a function of the CO₂ pressure. Their conclusion was that the reaction rapidly becomes diffusion controlled and that the pressure dependence of the diffusion-controlled reaction approximates that expected for a Langmuir adsorption isotherm. Unless it is possible to minimize the influence of the diffusion-controlled regime [3], it appears that the reaction of low surface area commercial CaO with CO₂ would take a long time before reaching an industrially acceptable degree of carbonation. Studies carried out in these laboratories have dealt with the influence of LiCl [4], LiBr [5], and NaCl, Li₂CO₃, CaCl₂ [6] on the kinetics of calcite decomposition. At high CO₂ pressure, the additives increase the initial decomposition rate by 2-5 times, presumably because liquid phase reaction paths are provided by the additives. It can be hoped that a liquid phase may have an even greater influence on the CaO-CO₂

recombination rate if the liquid prevents formation of a protective calcite coating on the CaO.

This paper reports the effects of Li_2CO_3 on the rate of reaction of CO_2 with low surface area CaO at temperatures below, near, and above the Li_2CO_3 - CaCO_3 eutectic (935 K) [7]. The kinetic measurements were supplemented by observation of morphologies, BET surface area measurements, and measurements of heat effects in a differential thermal analysis (DTA) apparatus.

EXPERIMENTAL

Mallinckrodt reagent grade CaO powders of about 3 μm particle size were used throughout the experiments. The powders were found to be about 30% hydrated and dehydration at 673 K was carried out with or without the additive before any carbonation experiments were made. After the dehydration, the surface area of the powder was found to be $\sim 6 \text{ m}^2/\text{g}$ by the BET method using an N_2 -He gas mixture.

For some runs, the samples were heated in air to 1473 K before they were mixed with Li_2CO_3 . Li_2CO_3 powders were intimately mixed with the CaO particles in different percentages.

Differential thermal analysis and thermogravimetric experiments were done simultaneously using alumina crucibles in a Netzsch apparatus. The thermogravimetric system was evacuated initially and then CO_2 gas was introduced. Pressure was controlled using a single side absolute sensor head plus a control system placed at the top of the microbalance. Constant heating rates of $0.2^\circ\text{C}/\text{min}$, $2^\circ\text{C}/\text{min}$, $5^\circ\text{C}/\text{min}$, and $10^\circ\text{C}/\text{min}$ were used in different experiments. The sensitivity of the microbalance was set at 2.5×10^{-3} gram/cm and that of the DTA was 0.1 mV at full scale.

Isothermal weight changes were measured in the same apparatus. CO_2 gas was introduced as soon as the temperature reached the preselected value. The Pt-Pt/Rd thermocouple tip projected upward into a 5 mm long recess in the bottom of the crucible. Differential thermal analyses were made on mixtures of Li_2CO_3 - CaCO_3 , Li_2CO_3 -CaO, and Li_2CO_3 - CaCO_3 -CaO in dry N_2 .

Morphological observations on starting materials and products were made with an ISI-130 scanning electron microscope (SEM) which can resolve to ~ 3 nm. The samples were coated with a ~ 2 nm layer of gold to prevent electron charging in the specimen.

RESULTS AND DISCUSSION

Figure 1 illustrates the typical data obtained from the microbalance when the heating rate was set at $5^\circ\text{C}/\text{min}$. The CO_2 pressure was about 4000 Pa and the Li_2CO_3 content was 7 wt% of the mixture of Li_2CO_3 and CaO. In the same figure, for comparison, the behavior of the same quantity of pure CaO has been plotted. The degree of carbonation of CaO is always increased by the presence of Li_2CO_3 . At 913 K, where the DTA shows a marked exothermic effect, the rate of reaction increases rapidly. This run was terminated when the sample reached 973 K, where calcite becomes unstable in CO_2 at 4000 Pa pressure [9]. The same kind of experiments carried out at higher CO_2 pressure (26,664 Pa), however, proved that the degree of carbonation reaches a limit dependent upon the heating rate (Table I); namely, the faster the heating rate, the lower the recorded final degree of carbonation. Heating at the same rates for more than 150°C higher than the temperature of the exothermic DTA peak caused negligible increases in the degree of reaction.

According to the literature [7], Li_2CO_3 and CaCO_3 form a eutectic phase which melts at 935 K. The maximum rate of carbonation is at measured temperatures which, depending on heating rates, lie 10 to 30°C below this eutectic (Table I). The reaction is exothermic, and the true temperatures at the reaction interface must be higher than the temperature recorded at the bottom of the crucible with the thermocouple. Probably the highest reaction rates reflect the formation of the Li_2CO_3 - CaCO_3 eutectic liquid phase.

To explore this possibility, CaO particles were first carbonated to 21%. Then they were mixed with Li_2CO_3 (24 wt%) and treated again in CO_2 with a heating rate of 10°C/min. The results (Table I) show that the rapid gain in weight occurred at 923 K, very near indeed to the carbonate eutectic temperature.

The CaCO_3 - Li_2CO_3 eutectic was heated in CO_2 in the absence of CaO. Negligible reaction between CO_2 and the eutectic liquid phase was observed. Furthermore, DTA analysis on the ternary system Li_2CO_3 - CaCO_3 -CaO in the absence of CO_2 and in the same range of temperature showed no thermal effects that might be connected with a ternary liquid phase.

As a step in gaining more insight into the reaction mechanism, the effects of different amounts of additive were studied. Figure 2 shows the results of isothermal thermogravimetric experiments carried out at 963 K and at CO_2 pressure equal to 4000 Pa. The isotherms show very rapid initial rates, almost independent of the amount of Li_2CO_3 added, followed by slower rates. These experiments (Fig. 2) and others [6] showed that the maximum carbonate formation produced when almost 10% Li_2CO_3 was present.

Insights into the influence of Li_2CO_3 on the CaO-CO_2 reaction can be obtained by taking into account the phase diagram (Fig. 3), although it must be remembered that sample compositions are not perfectly homogeneous so that local regions may be closer in composition than the averages are to the eutectic composition, 43 wt% CaCO_3 . An important fact to note is that as the amount of Li_2CO_3 is increased, an increased quantity of CaCO_3 must be formed before the eutectic composition is reached. For instance, the 7% Li_2CO_3 mixture needs only 3.2% reaction of CaO , while the 50% Li_2CO_3 mixture requires 22.7% reaction. Consequently, when lower percentages of Li_2CO_3 are present, most of the CaO-CO_2 reaction occurs in the presence of $\text{CaCO}_3(\text{s})$ and a carbonate liquid phase (region A in Fig. 3), with more Li_2CO_3 present, reaction occurs largely in the presence of $\text{Li}_2\text{CO}_3(\text{s})$ and the Li_2CO_3 -saturated liquid phase (region B in Fig. 3).

Under the experimental conditions adopted, the additive does not undergo significant vaporization. For reactions that occur in the CaCO_3 -rich region, all the Li_2CO_3 initially added will be liquid and CaCO_3 will be precipitated from a Li_2CO_3 - CaCO_3 liquid phase (point C in Fig. 3) from the beginning of the reaction to the end. Figure 4(a&b) show SEM observations of samples reacted up to 20% from a starting specimen prepared with 10 wt% of Li_2CO_3 . Since these pictures were taken at room temperature, a definite conclusion that calcite precipitates at high temperatures from the liquid phase cannot be made; but the large calcite crystals seen in the pictures strongly suggest the recrystallization of the calcite.

Figure 5 shows a sample prepared from 57% Li_2CO_3 and reacted until 21% of the CaO formed calcite. No large calcite crystals are

present. When reaction is carried out in the Li_2CO_3 -rich region, all the CaCO_3 is liquid and the amount of the liquid phase (Li_2CO_3 - CaCO_3) increases from the beginning to the end of the reaction (point D in Fig. 3). Up to 63% of the CaO must react before the CaCO_3 starts to precipitate from the liquid phase. Therefore, no high-temperature recrystallization of calcite should occur.

It is possible to correlate the lower final degree of CaO-CO_2 reaction with a greater amount of liquid phase formed during the reaction. The observation that the mass of a Li_2CO_3 - CaCO_3 sample did not change when CO_2 was introduced into the system at 959 K indicates the solubility of CO_2 in the carbonate eutectic is very low. Consequently, although the liquid probably removes the CaCO_3 solid layers from the CaO surfaces, the liquid may itself act as a protective barrier to CO_2 transport to the CaO surface.

For a possible explanation of the data one might assume a multistep process for the reaction. The first step is the formation of a CaCO_3 layer on the CaO particles. As soon as CaCO_3 has reached the amount required at the local temperature for the formation of the liquid phase, the calcite formed on the CaO surface will dissolve as it forms and recrystallize as more stable larger calcite crystals, as long as the reaction occurs in the CaCO_3 -rich region. If the rate-limiting step is the diffusion of CaCO_3 or of CO_2 through the liquid phase, then the reaction rate would decrease as the liquid layer grows, although the rate would remain higher than that when a protective calcite layer is formed.

Figure 6b shows the typical morphology of samples carbonated in the CaCO_3 -rich region. The initial CaO particles (Fig. 6a) were about

3 μm size as irregular block-like shapes. These blocks were well separated but the carbonated particles show small blocks interconnected in the phase of viscous appearance. Within the viscous regions well-defined crystalline planes are visible as are a finer structure made up of what appear to be small regular cracks. Surface areas of these samples are less than $1 \text{ m}^2/\text{g}$. It is therefore concluded that the apparent fine cracks of those samples do not indicate a porous structure but rather a surface roughness.

The proposed mechanism would give an initial rate of isothermal reaction with Li_2CO_3 present that is equal to that without additive. Unfortunately, it is not easy to measure this value because a certain amount of CaCO_3 may be already formed on the CaO particles before isothermal conditions are reached. If so, the initial data plotted at 963 K (Fig. 2) could reflect a state where the Li_2CO_3 - CaCO_3 liquid phase is already active.

To overcome this difficulty, a "quasi-isothermal" experiment was designed. The heating rate was set equal to $0.2^\circ\text{C}/\text{min}$, and the CO_2 pressure was 26,664 Pa. This would allow observation of the relative reaction rates at low temperatures. In Fig. 7 the results are illustrated for the CaO particles with and without Li_2CO_3 (15%). Both samples behave similarly up to 633 K. Then the one with Li_2CO_3 starts to pick up CO_2 at a rapidly increasing rate and reaches 100% reaction. From the evidence that both samples initially have the same reaction rate, it follows that the formation of a certain quantity of CaCO_3 on the CaO particles is required before the additive effect is observed.

It is interesting to note that some enhancement of the rate of the CaO - CO_2 reaction is caused by Li_2CO_3 as much as 250°C below the

Li_2CO_3 - CaCO_3 eutectic melting point. Since DTA analysis on the CaO - Li_2CO_3 systems in dry N_2 and in the same range of temperature showed no thermal effects that might be connected with a liquid phase, this enhancement must be due to a solid-state or surface phenomenon.

The microstructural features of samples carbonated in this temperature regime strongly support a different reaction path. Fig. 8(c&d), taken on CaO particles containing 12.6% Li_2CO_3 and carbonated at 779 K up to 19.5% under a CO_2 pressure of 12132 Pa, shows that the particles are sintered and the grain boundaries are well developed. The grain surface shows fine cracks similar to those observed in higher-temperature samples. The low specific surface area, less than $1 \text{ m}^2/\text{g}$, implies that the CaCO_3 coating layer is not porous.

As shown in Fig. 8(a&b), the coating on CaO particles with Li_2CO_3 seems to have much smaller crystallites than coatings obtained without Li_2CO_3 . Similar grain size decreases are produced in MgF_2 by small additions of CaF_2 [8]. In this low-temperature regime, the increase in reaction rate when Li_2CO_3 is present may be a consequence of increased CO_2 permeation along an intergranular path. Experiments are currently underway to test this hypothesis.

CONCLUSIONS

The effect of Li_2CO_3 on the rate of reaction of CO_2 with low surface area CaO powders has been found to be strongly influenced by the eutectic phase between CaCO_3 and Li_2CO_3 . The reaction rates and product morphologies are different in three regimes: At temperatures where the Li_2CO_3 - CaCO_3 eutectic phase can form, the CaCO_3 , which forms a protective coating on CaO , is dissolved and reprecipitated as large

CaCO_3 crystals, and the reaction proceeds on the CaO surface with a high rate. If enough Li_2CO_3 is present so that the liquid does not become saturated with CaCO_3 , the liquid content of the sample increases as reaction proceeds and the liquid phase itself acts as a protective coating. Below the eutectic temperature, Li_2CO_3 additions decrease the grain size of the polycrystalline CaCO_3 coating layer, and an increase in reaction rate occurs, probably because the increased number of grain boundaries provide additional paths for intergranular diffusion to the CaO .

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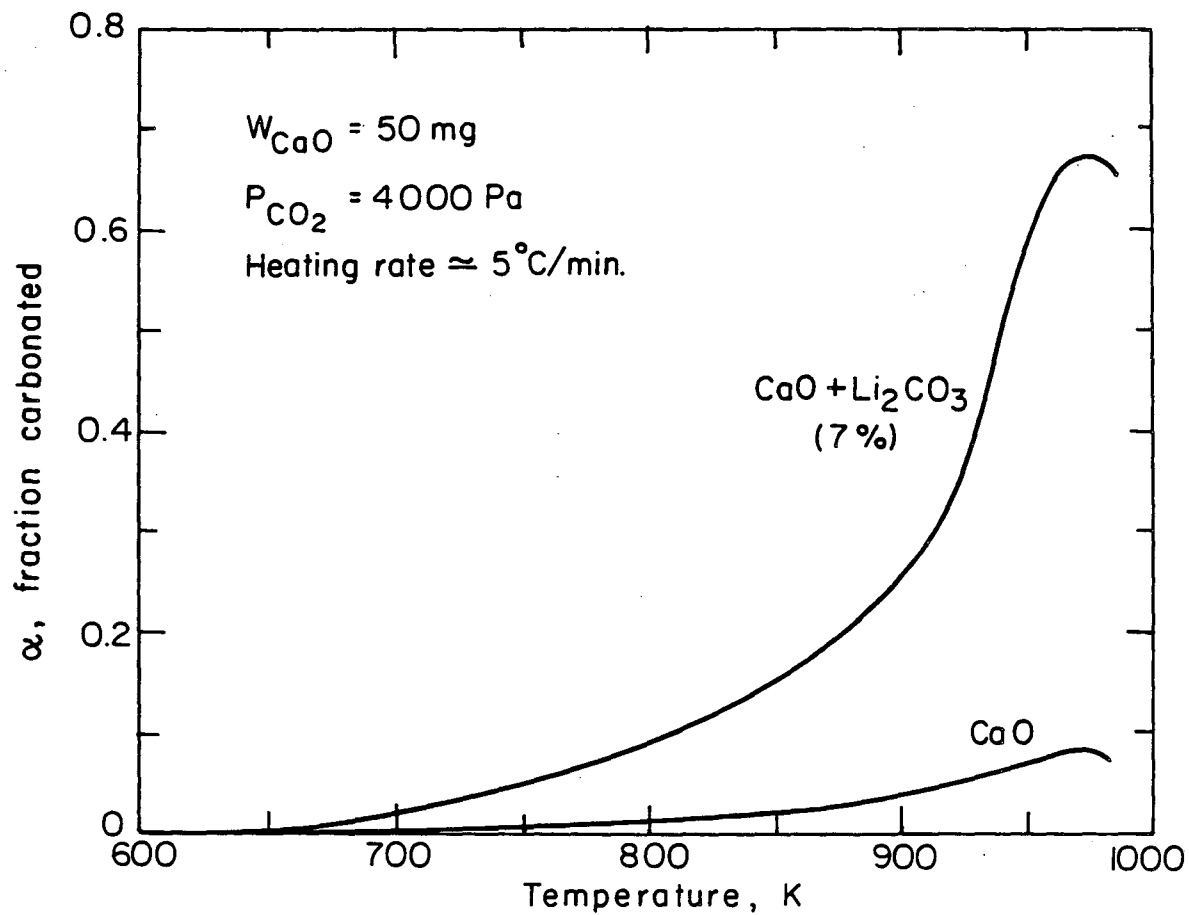
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Table I. Influence of heating rate on maximum reaction rate and on final degree of carbonation.

Samples	Heating rate (°C/min)	CO ₂ préssures (Pa)	Temperature corresponding to maximum in the DTA traces (K)	Degree of carbonation when rate became negligible (%)
CaO-Li ₂ CO ₃ (7%)	5	4,000	913	65
CaO-Li ₂ CO ₃ (15%)	10	26,664	893	70
CaO-Li ₂ CO ₃ (15%)	2	26,664	903	81
CaO-Li ₂ CO ₃ (15%)	0.2	26,664	913	100
CaO-Li ₂ CO ₃ (53%)	10	26,664	923	60
CaO-CaCO ₃ -Li ₂ CO ₃ (21%) (24%)	10	26,664	923	34

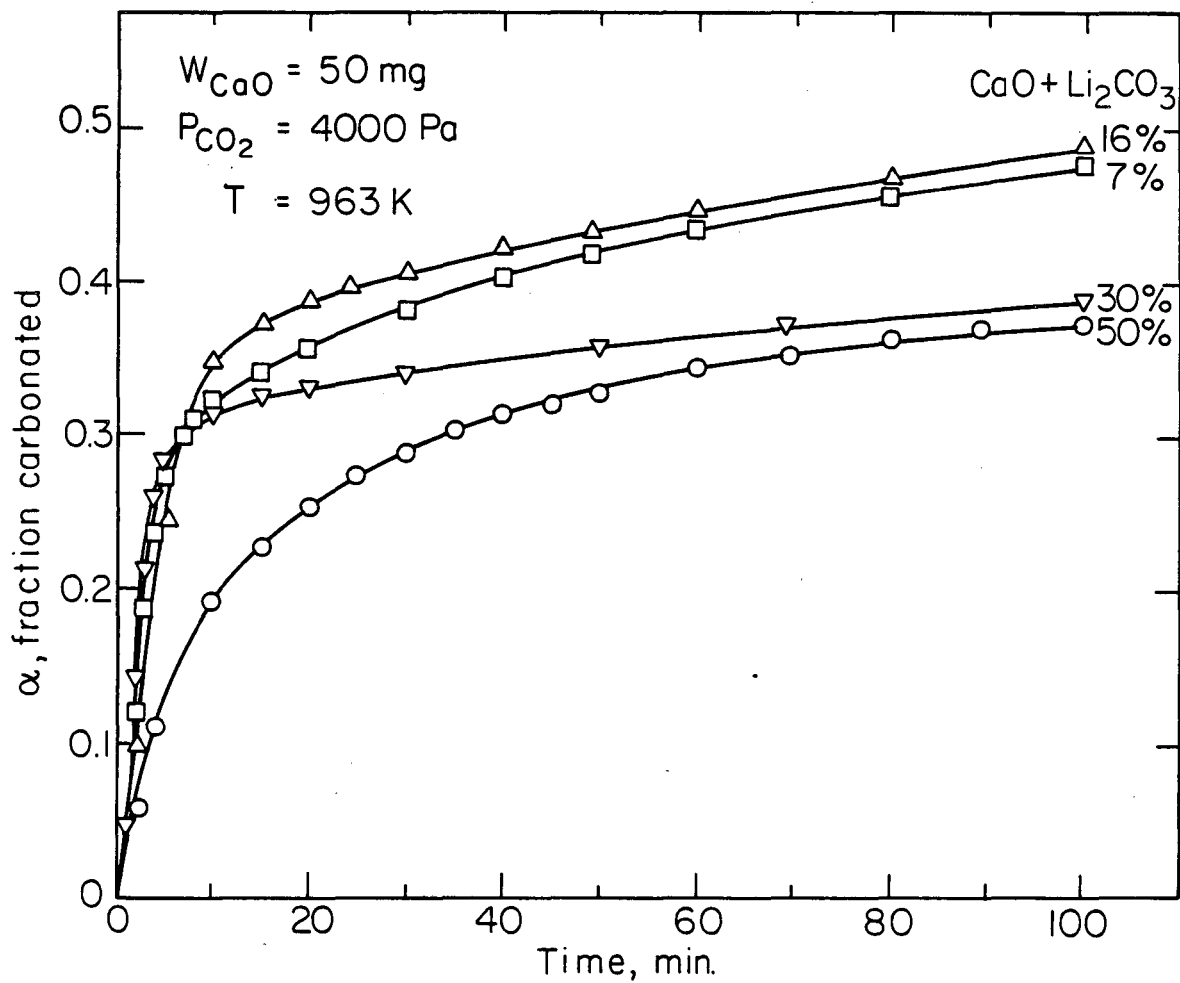
Figure Captions

- Fig.1 The dynamic carbonation of CaO with 7% Li_2CO_3 and without Li_2CO_3 .
- Fig.2 The isothermal carbonation of CaO with various compositions of Li_2CO_3 at 963 K.
- Fig.3 The phase diagram of Li_2CO_3 - CaCO_3 system from Ref. 7. The line ---- indicates the experimental temperature.
- Fig.4 20% carbonated sample with 10% Li_2CO_3 heated at 963 K in 4000 Pa of CO_2 .
- Fig.5 CaO carbonated with 57% Li_2CO_3 at 963 K and 4000 Pa of CO_2 .
- Fig.6 (a) The vacuum dehydrated initial CaO particles.
(b) The carbonated CaO with 9.5% Li_2CO_3 at 963°K and 4000 Pa of CO_2 .
- Fig.7 The dynamic carbonation of CaO with 15% Li_2CO_3 and without Li_2CO_3 .
- Fig.8 CaO carbonated without Li_2CO_3 (a&b) and with 12.6% Li_2CO_3 (c&d) at 779 K and 12132 Pa of CO_2 .



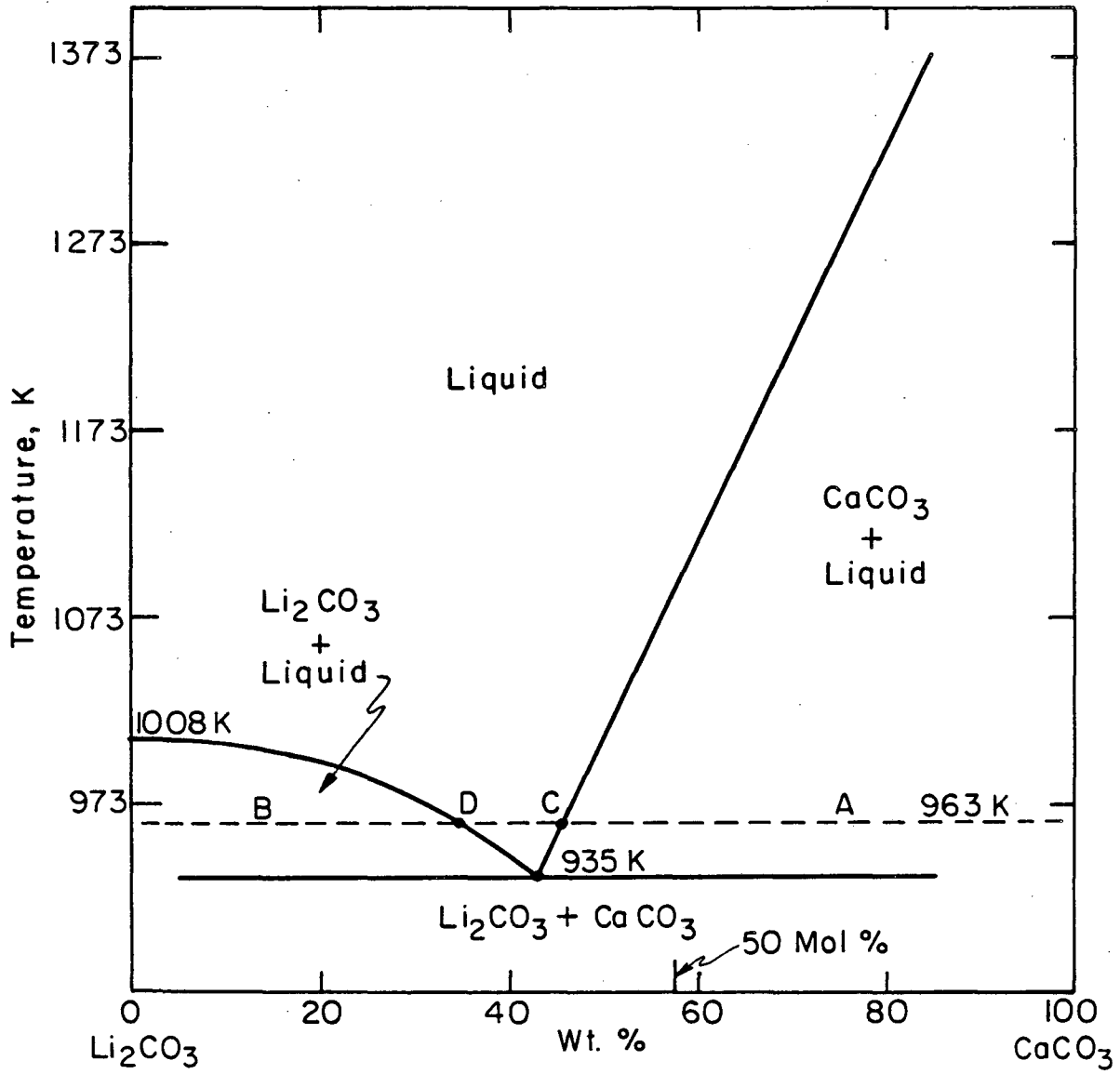
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Figure 1



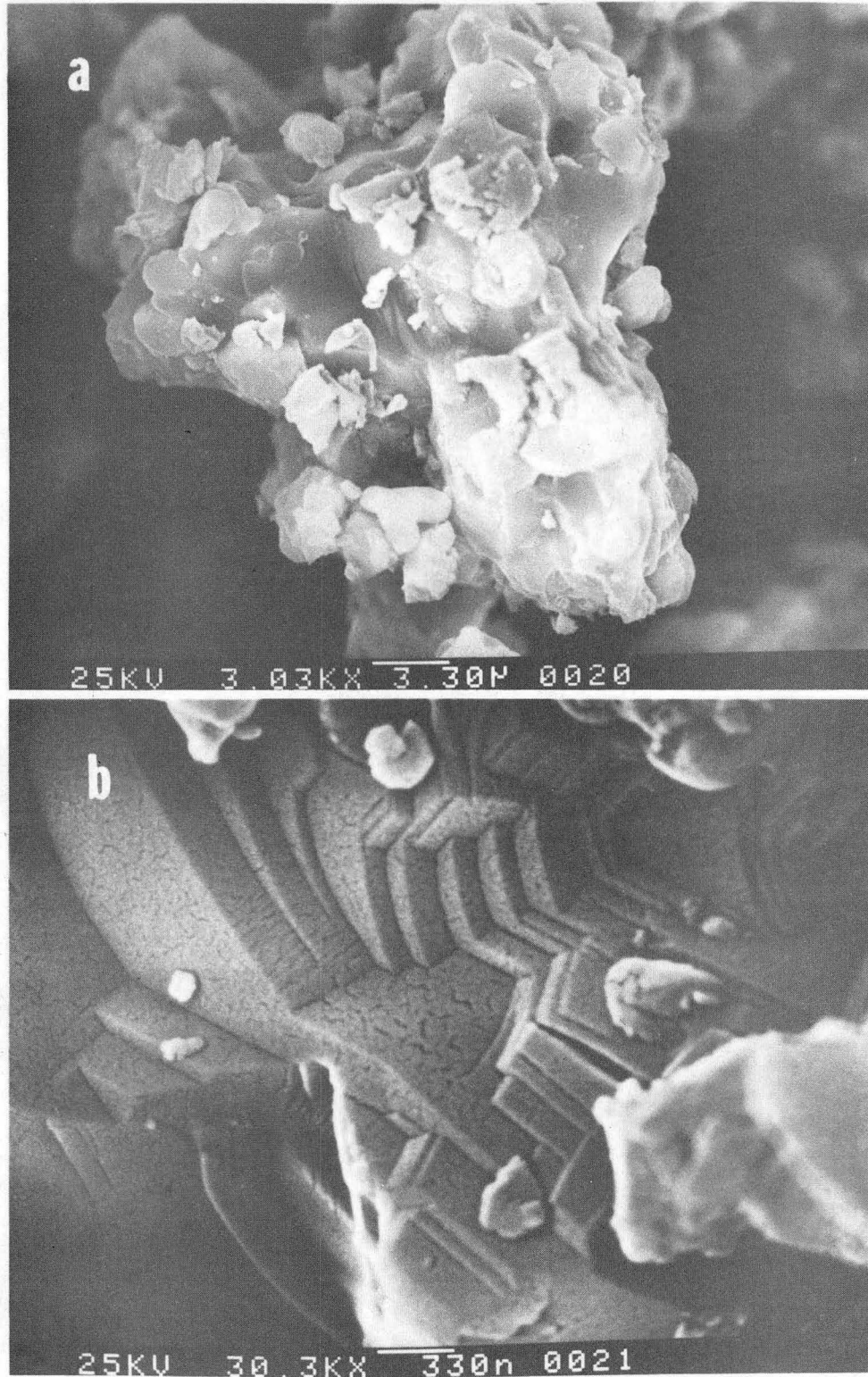
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Figure 2



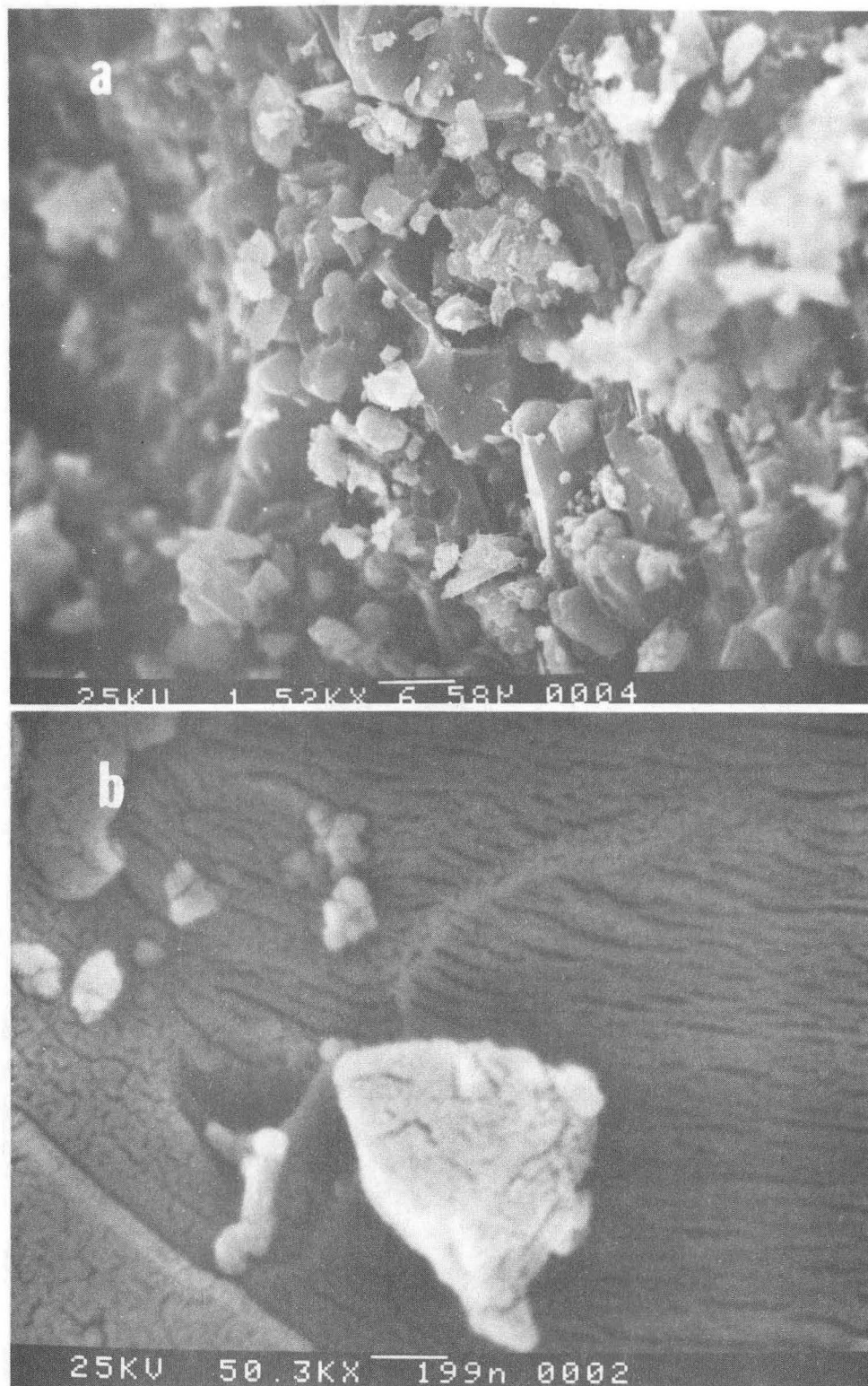
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Figure 3



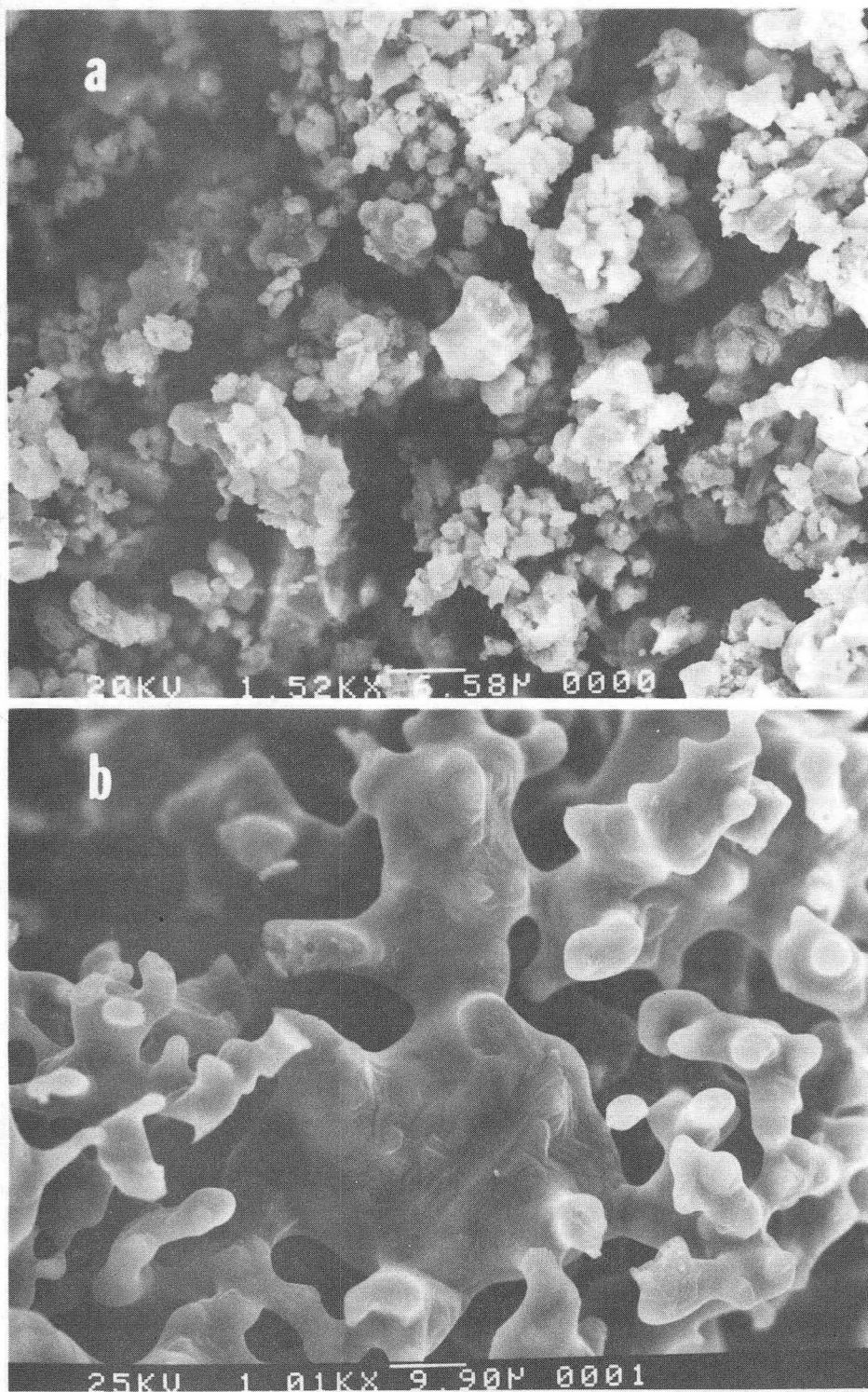
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Figure 4



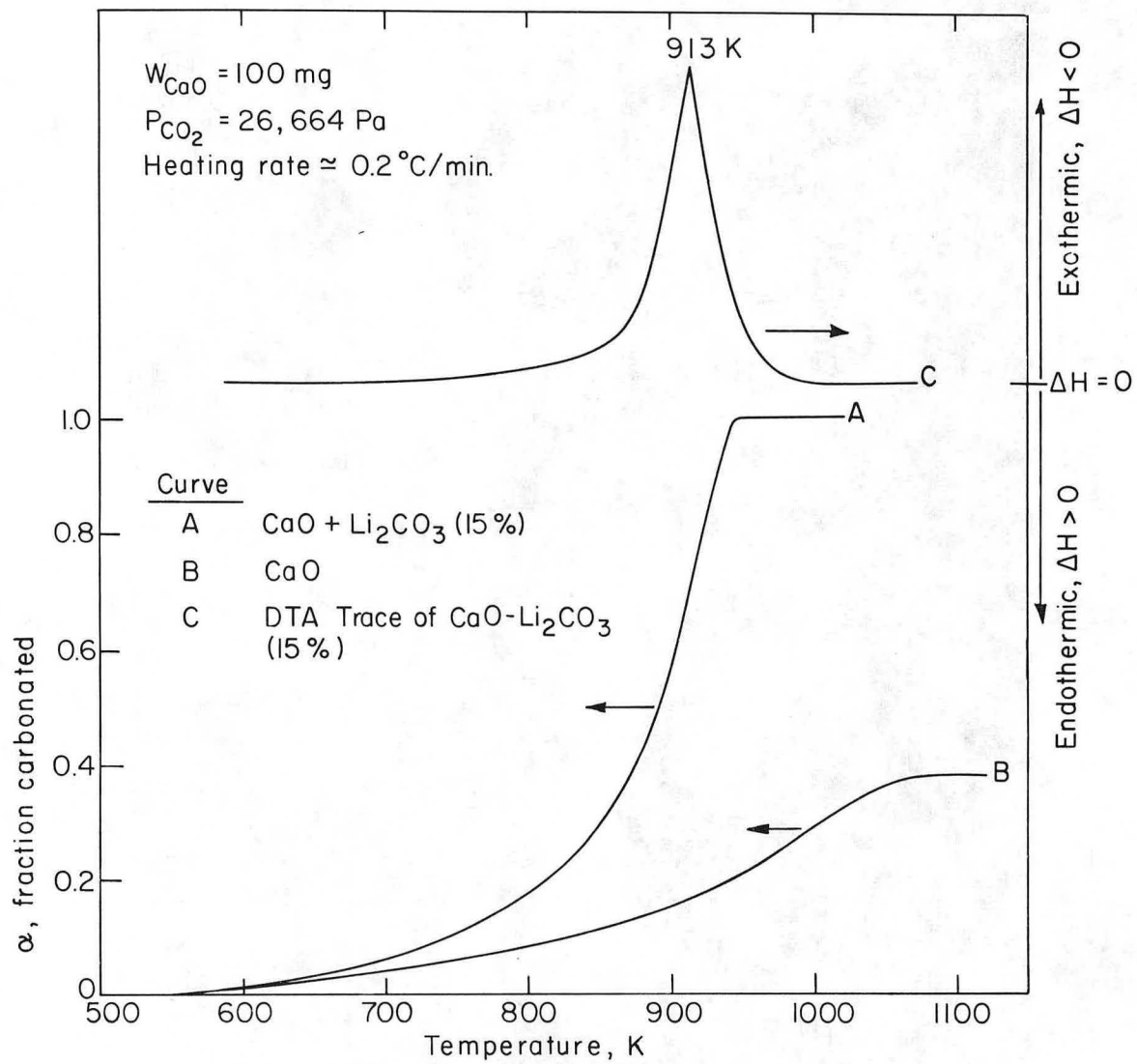
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Figure 5



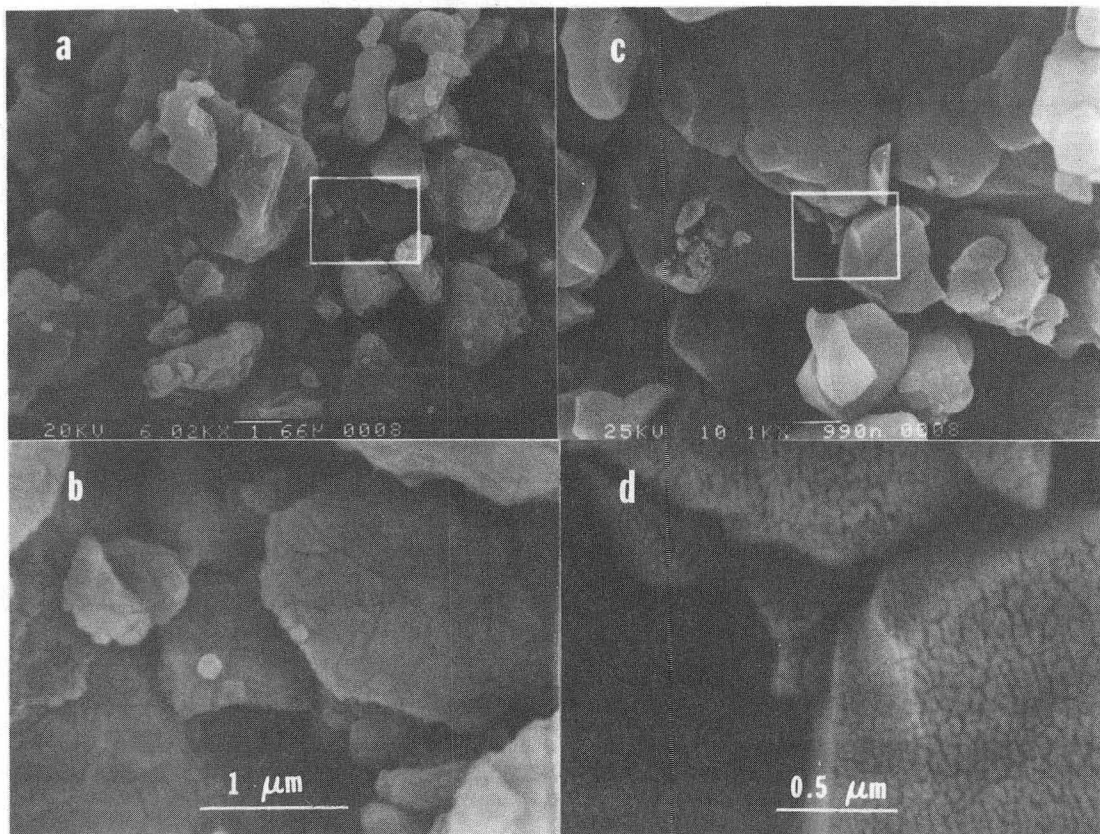
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Figure 6



XBL 837-6041

Figure 7



XBB 837-6359

Figure 8

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