Thermochimica Acta, 122 (1987) 23-28
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

INVESTIGATION OF THE THERMAL STABILITY OF $CaCO_3$-$SrCO_3$ SOLID SOLUTIONS

B. FUBINI,[1] F. DI RENZO[2] and F.S. STONE[3]

[1]Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Torino, Via P. Giuria 9, 10125 Torino (Italy)

[2]Dipartimento di Chimica Industriale ed Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)

[3]School of Chemistry, University of Bath, Bath BA2 7AY (UK)

ABSTRACT

The decomposition of solid solutions of $CaCO_3$-$SrCO_3$, covering the whole range of composition, has been studied by simultaneous TG-DTA. In all cases a two-stage decomposition occurs and the presence of strontium stabilizes $CaCO_3$.

The effect of the different amounts of calcium and strontium ions present in the samples has been separately evaluated by comparison with the results obtained by decomposing mechanical mixtures of $CaCO_3$ and $SrCO_3$ of the same composition.

INTRODUCTION

The thermal decomposition of metal carbonate solid solutions to the corresponding oxides often occurs in two stages because of the different thermal stabilities of the two carbonate components (ref. 1). This can occur also when the final product is a solid solution, and investigation of this process in systems where miscibility of cations occurs over a wide range of composition has been carried out in our laboratories (ref. 2).

In the present paper, we report the results of a thermal analysis study on the effects of stabilization of the aragonite structure of $CaCO_3$ by introduction of strontium ions in solid solution, with due attention given to possible interfering effects of sample weight. Detailed investigation of the thermochemistry and kinetics of decomposition as a function of Sr content will be reported in a later paper, together with results on the phase transitions in the $CaCO_3$-$SrCO_3$ system (ref. 3).

EXPERIMENTAL

$Sr_xCa_{1-x}CO_3$ solid solutions were prepared in finely-divided form in the whole range of composition by precipitation from solutions of the mixed nitrates under conditions of vigorous stirring (ref. 4). All the solids exhibited the aragonite-strontianite structure but at Sr concentrations below $x = 0.40$ traces of calcite could be detected by X-ray diffraction. Samples are designated according to mol % Sr: e.g., S40 signifies a sample with $x = 0.40$, etc.

0040-6031/87/$03.50

Mechanical mixtures of $CaCO_3$ and $SrCO_3$ were made by mixing together the requisite amounts of calcite-phase $CaCO_3$ (Carlo Erba) and $SrCO_3$ (Carlo Erba). It is not significant that calcite $CaCO_3$ rather than aragonite $CaCO_3$ was used, since if the latter had been employed the phase transition to calcite would have been complete well below the temperature range (550-1050°C) with which the present work is concerned.

Decompositions of the carbonate solid solutions and mechanical mixtures were performed in a coupled TG-DTA Mettler TA 2000C apparatus in flowing nitrogen using samples of 12.5 mg unless otherwise stated.

RESULTS AND DISCUSSION

To illustrate the typical two-stage decomposition behaviour of the solid solutions, Fig. 1 shows the simultaneous TG-DTA trace for the solid solution

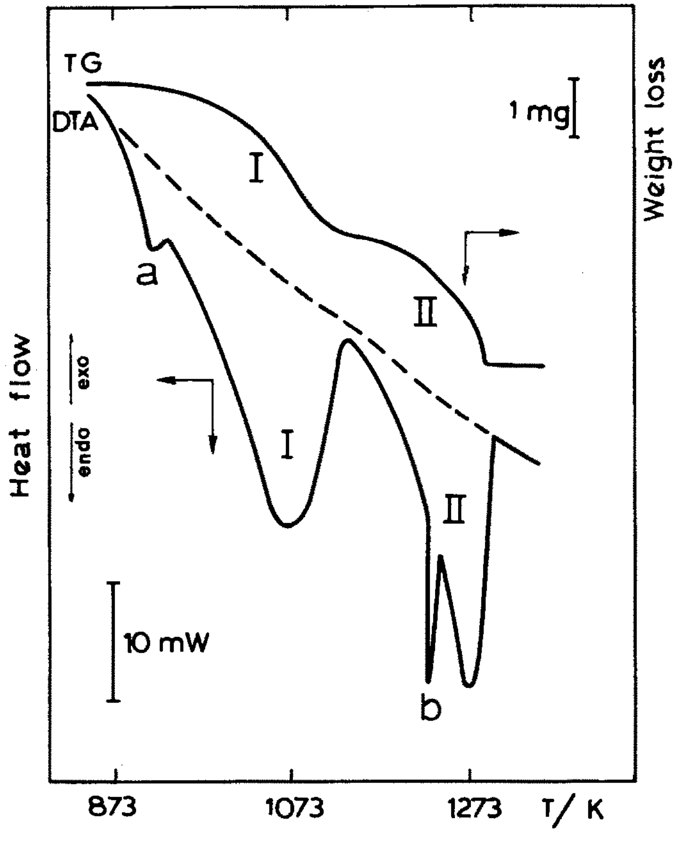

Fig. 1. TG-DTA trace for solid solution S40 ($Sr_xCa_{1-x}CO_3$ with x = 0.40). Experimental conditions: weight 14 mg, heating rate 20 K min^{-1}, flowing N_2. For marked symbols see text.

containing 40 mol % $SrCO_3$. Phase analysis after the first decomposition shows the presence of an oxide phase and a carbonate phase in which the cations have become largely de-mixed as CaO and $SrCO_3$, respectively (refs. 2,3). Thus the feature marked as I is due mainly to the decomposition of carbonate associated with calcium and that as II with carbonate associated with strontium. Detailed analysis of weight losses and X-ray diffractograms (refs. 2,3) reveals that the above description is not entirely clear-cut; for instance, after the first decomposition some Ca is found to be retained in the residual carbonate phase. The two small endotherms marked a and b at 640°C (913 K) and 950°C (1223 K), respectively, which are superimposed on the decomposition endotherms, are not accompanied by a weight loss, and are due to phase transitions which will be discussed elsewhere (ref. 3).

Fig. 2 shows DTG results for the three representative solid solutions (S20, S50 and S80) compared with DTG data for the same weights of the corresponding mechanical mixtures. Thus, for comparison with the solid solution of composition $Sr_xCa_{1-x}CO_3$, $xM_{Sr}\alpha w$ g of $SrCO_3$ was mixed with $(1-x)M_{Ca}\alpha w$ g of $CaCO_3$, where M_{Sr} and M_{Ca} are the molecular weights of $SrCO_3$ and $CaCO_3$, respectively, $\alpha = [xM_{Sr} + (1-x)M_{Ca}]^{-1}$, and w was the total weight required (12.5 mg).

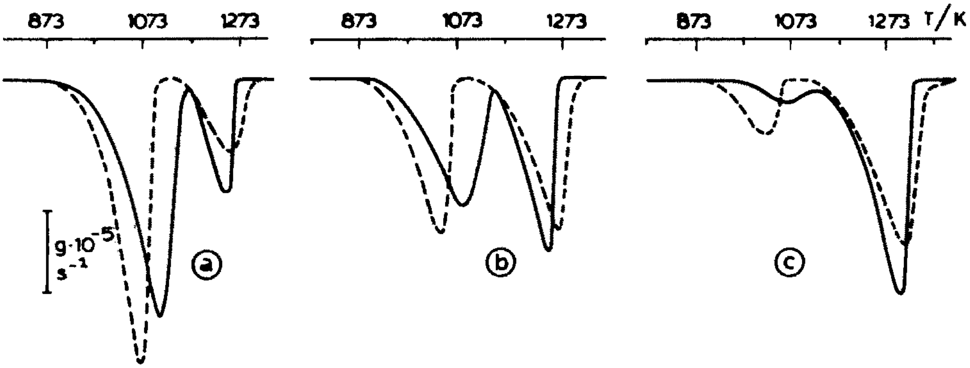

Fig. 2. DTG traces of solid solutions (a) S20, (b) S50 and (c) S80 (continuous lines) and corresponding mechanical mixtures of $CaCO_3$ and $SrCO_3$ (dashed lines). Experimental conditions: weight 12.5 mg, heating rate 20 K min^{-1}, flowing N_2.

Two main differences between solid solutions and mechanical mixtures are clearly seen from Fig. 2:

(a) in comparison with the mechanical mixture, the peak of the first decomposition is displaced to higher temperature in the solid solutions and the peak width is greater;

(b) the second decomposition peak is sharper in the solid solution than in the mechanical mixture.

Carbonate ions associated with calcium will be stabilized when in the solid solution because of adjacent strontium. The decomposition in the first stage may therefore be expected to be different from that of decomposition of pure $CaCO_3$, and to occur at a slower rate. The $SrCO_3$ phase resulting after the first decomposition of the solid solution is in a finely-divided form, as shown by an increased breadth of X-ray reflections compared to the starting material (ref. 3). This implies increased reactivity, and explains why the second decomposition occurs more rapidly than with the pure $SrCO_3$.

Fig. 3 shows the temperature of the onset of decomposition as a function of composition. A marked dependence of decomposition onset upon strontium content is detected in the solid solution, and this effect is particularly evident when Sr prevails, i.e. beyond 50% in Sr. The degree of stabilization of the solid solutions can be seen by comparing the onset of decomposition with the results of the corresponding $CaCO_3$-$SrCO_3$ mechanical mixtures. Fig. 3 also includes data obtained for the decomposition of pure $CaCO_3$ (i.e. without admixed $SrCO_3$) in amounts equal to the amount of $CaCO_3$ in the corresponding mechanical mixtures. These data confirm that the onset temperature of decomposition is unaffected by the presence of non-decomposing $SrCO_3$. Returning to the solid solution results,

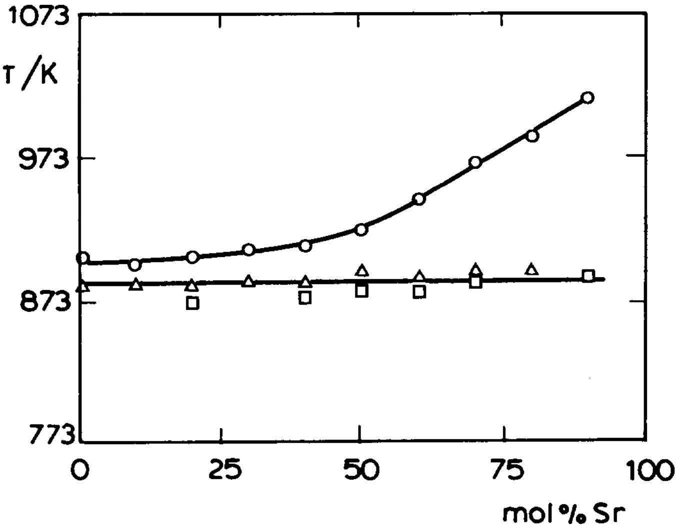

Fig. 3. Onset temperatures of first stage decomposition. (o) Solid solutions, (□) Mechanical mixtures. Onset temperature measured as the temperature at which a 12.5 mg sample lost 0.02 mg weight. (△) Samples of $CaCO_3$ alone with weights corresponding to the amounts of $CaCO_3$ in the corresponding mechanical mixtures (see text). Onset temperatures measured for 0.02 mg weight loss. Experimental conditions: heating rate 20 K min^{-1}, flowing N_2.

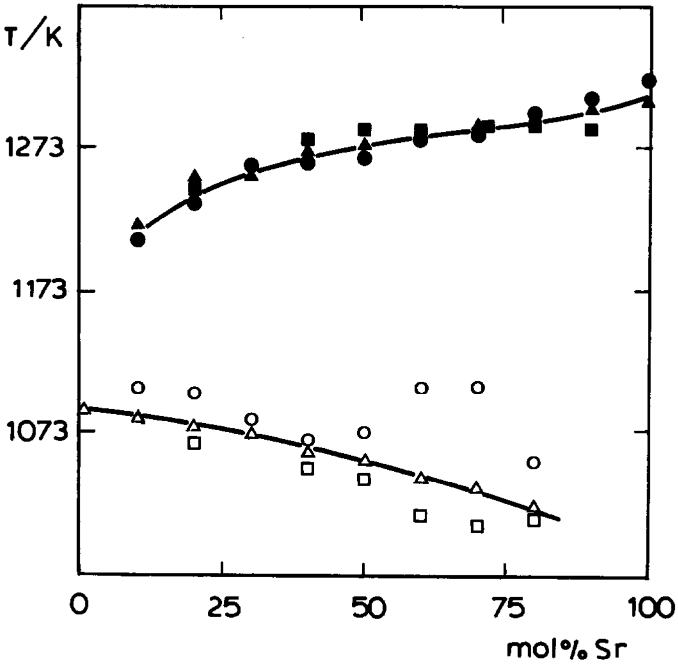

Fig. 4. Temperature of maxima of decomposition peaks. First stage decomposition (open symbols) and second stage decomposition (filled symbols) for solid solutions (circles) and mechanical mixtures (squares), together with decomposition peaks for the component amounts of pure $CaCO_3$ (open triangles) or $SrCO_3$ (filled triangles) when measured separately as unmixed solids. Experimental conditions as for Fig. 3.

the near-constancy of the onset temperature up to 40 mol % Sr is probably a reflection of the presence of the small quantities of calcite impurity, as mentioned previously.

Fig. 4 shows in detail the comparison of the peak temperatures of decompositions I and II for the solid solutions and the mechanical mixtures. Data for the decompositions of the corresponding amounts of pure $SrCO_3$ alone (upper part of Fig. 4) or pure $CaCO_3$ alone (lower part) are also included.

In contrast to the onset temperatures, it is seen that the peak temperatures for the respective decompositions of $CaCO_3$ and $SrCO_3$ decrease with decreasing amount of carbonate decomposing (open triangles, left to right, for decreasing $CaCO_3$; filled triangles, right to left, for decreasing $SrCO_3$). This is an artefact, well known in thermal analysis (ref. 5), and the data for the solid solutions and the mechanical mixtures need to be considered against this background.

As regards the first decomposition stage (lower part of Fig. 4), the plot shows that the peak temperature for the solid solution is consistently higher than the peak temperature for the corresponding mechanical mixture, and that there is a particularly large difference when the strontium content is above 40 mol %. It more than compensates for any effect caused by the decreasing amount of calcium in the sample, and confirms absolutely that there is a genuine effect of stabilization by strontium. It is interesting that data for the mechanical mixtures lie below those for the decomposition of the same amounts of $CaCO_3$ studied separately as unmixed $CaCO_3$. We suggest that dilution by admixed $SrCO_3$ (which is inert at temperatures below 900°C) lowers the effective partial pressure of CO_2 at the surface of reacting $CaCO_3$ particles and the consequent increase in rate of decomposition lowers the peak temperature.

In the case of the second decomposition stage (upper part of Fig. 4), we note that the points for all samples studied fall on the same curve. The near-coincidence of the points for the solid solutions and the mechanical mixtures is entirely consistent with the conclusion from phase analysis work that the material remaining after the first decomposition in the solid solution case is largely-demixed $SrCO_3$.

REFERENCES

1 Z.M. Zemtsova, E.A. Prodan and M.M. Pavlyuchenko, Russ. J. Phys. Chem., 51 (1977) 1406.

2 B. Fubini and F.S. Stone, Mater. Sci. Monographs, Vol. 28, p.85, Elsevier, Amsterdam, 1985.

3 B. Fubini, F.S. Stone and F. Di Renzo, to be published.

4 M.M. Ramirez de Agudelo and F.S. Stone, Mater. Sci. Monographs, Vol. 10, p.695, Elsevier, Amsterdam, 1982.

5 A. Blazek, "Thermal Analysis", p.37, van Nostrand Reinhold, London, 1973.