Solid-state Reaction between Strontium Carbonate and Silica

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Metastable $SrSiO_3$ was formed during the course of the reaction between an equimolar mixture of $SrCO_3$ and SiO_2. The reaction was found to proceed in four stages, (1)—(4). The overall reaction of (1) and (2) was best described

$$2\,SrCO_3 + SiO_2 \longrightarrow Sr_2SiO_4 + 2\,CO_2 \qquad (1)$$

$$SrCO_3 + SiO_2 \longrightarrow SrSiO_3\text{ (metastable)} + CO_2 \qquad (2)$$

$$SrSiO_3\text{ (metastable)} \xrightarrow{\text{transformation}} SrSiO_3\text{ (stable)} \qquad (3)$$

$$Sr_2SiO_4 + SiO_2 \longrightarrow 2\,SrSiO_3\text{ (stable)} \qquad (4)$$

by the Jander equation and the apparent activation energy was determined as 215.5 kJ mol^{-1} irrespective of the ball-milling time. The increase in the reactivity caused by ball-milling was confirmed by thermal analysis (t.g.a. and d.t.a.). The effect of ball-milling is possibly interpreted in terms of the decrease in particle size of $SrCO_3$ in the early stages and of the improvement of SiO_2 dispersion in the later stages. The rate of formation of stable $SrSiO_3$ from Sr_2SiO_4 and SiO_2 [reaction (4)] was determined. Reaction isotherms were best expressed by the Ginstling–Brounshtein equation and the activation energy was 510 kJ mol^{-1}.

STRONTIUM silicate exists in three forms: $SrSiO_3$, Sr_2SiO_4, and Sr_3SiO_5. Although the final product can be predicted from the starting composition by referring to the equilibrium phase diagram, more than one compound is often observed during reactions in silicate systems. Jander and Wuhrer [1] studied the reaction between $SrCO_3$ and SiO_2 and suggested that Sr_2SiO_4 is always the first product formed from the mixture at any Sr : Si ratio. Glushkova and Keler [2] supported the preferential formation of Sr_2SiO_4 regardless of the starting composition and reported that the formation of $SrSiO_3$ by the reaction of SiO_2 with Sr_2SiO_4 from a mixture with Sr : Si = 1 : 1 proceeds slowly at 1 280 °C, and it is completed rapidly at 1 320 °C. On the other hand, although $SrSiO_3$ has been known only in the pseudo-wollastonite modification,[3] Takahashi and Roy [4] suggested that a new metastable modification is obtained by heating the $SrSiO_3$ glass. Moreover, we have reported [5] that this compound is crystallised at 850—910 °C from the mixed powder prepared by the alkoxy-method.

In the present study, it was found that metastable $SrSiO_3$ is formed during the course of the reaction between an equimolar mixture of $SrCO_3$ and SiO_2. On the basis of this result, a systematic investigation has been carried out. The kinetic data were analysed with use of the available solid-state models.

EXPERIMENTAL

Reagent-grade chemicals were used throughout as starting materials. Strontium carbonate and amorphous SiO_2 were heated for 3 h at 500 and 600 °C, respectively. An equimolar mixture was weighed, and then ball-milled together in a polyethylene pot containing agate balls for 20, 90, and 190 h. No liquid medium was used. The particle size of $SrCO_3$, as determined by electron microscopy, is given in Table 1. The particle size of amorphous SiO_2 remained virtually constant during ball-milling, and was 0.05—0.08 μm.

Differential thermal analysis (d.t.a.) was carried out in air at a rate of 10 °C min^{-1}. Alpha-alumina was used as a standard material. The specimens heated at 10 °C min^{-1} were examined by high-temperature *X*-ray diffraction using nickel-filtered Cu-K_α radiation. The overall reaction concerning the decomposition of $SrCO_3$ has been analysed by measuring the weight decrease as a function of time with a thermobalance. Free SrO was not detected throughout the heating process. The fractional formation of stable $SrSiO_3$ (pseudo-wollastonite modification) was determined from the height of the main characteristic peak, d = 3.57 Å (ref. 6), by means of a standard *X*-ray diffractometer, using a calibration curve prepared with known compositions.

TABLE 1

Effect of ball-milling on the particle size of $SrCO_3$

Starting powder	Ball-milling time/h	Particle size/ μm	Average size ratio $\bar{r}_{SrCO_3}/\bar{r}_{SiO_2}$
A	20	0.7—2.1	24
B	90	0.2—0.9	10
C	190	0.1—0.5	7

RESULTS AND DISCUSSION

Differential Thermal Analysis.—Figure 1 shows a d.t.a. curve of the starting powder A. Four reactions were observed at 730—890 °C, 890—980 °C, 990—1 060 °C, and above 1 180 °C. The *X*-ray diffraction analysis confirmed that the large peak (730—980 °C) comprising two successive endothermic peaks (730—890 and 890—980 °C) is due to the formation of Sr_2SiO_4 and metastable $SrSiO_3$, respectively, associated with the decomposition of $SrCO_3$. On the other hand, the first exothermic peak (990—1 060 °C) was found to be due to the transformation of metastable into stable $SrSiO_3$, and the second (above 1 180 °C) to the formation of stable $SrSiO_3$ by the reaction between Sr_2SiO_4 and SiO_2.

X-*Ray Analysis.*—Identified phases for specimens at various temperatures are given in Table 2. No products were obtained up to 710 °C. The peaks corresponding to Sr_2SiO_4 began to appear at 730 °C, and the intensity increased up to 980 °C. Strontium orthosilicate (Sr_2-

TABLE 2

Phases identified for specimens of $SrCO_3 + SiO_2$ heated at various temperatures

Temperature/°C	Phase
730—860	$SrCO_3$, Sr_2SiO_4
860—980	$SrCO_3$, Sr_2SiO_4, metastable $SrSiO_3$
980—990	Sr_2SiO_4, metastable $SrSiO_3$
990—1 060	Sr_2SiO_4, metastable $SrSiO_3$, stable $SrSiO_3$
1 060—1 350	Sr_2SiO_4, stable $SrSiO_3$
1 360	stable $SrSiO_3$

SiO_4), as in the results reported previously,[1,2] was the first product formed. Irrespective of the formation of Sr_2SiO_4, metastable $SrSiO_3$[4,5] was formed in the temperature range 860—910 °C. The peaks of $SrCO_3$ as a starting material disappeared at 980 °C. In addition, thermogravimetric examination showed the continuous weight loss due to the decomposition of $SrCO_3$ at 720—980 °C. It is evident therefore that the formation of Sr_2SiO_4 and metastable $SrSiO_3$ is associated with the decomposition of $SrCO_3$. Metastable $SrSiO_3$ was transformed into stable $SrSiO_3$ between 990 and 1 060 °C. After completion of the transformation, no change in the Sr_2SiO_4 and stable $SrSiO_3$ spectra was recognised up to 1 180 °C. The intensity of the peak due to stable $SrSiO_3$ increased gradually above 1 180 °C in inverse proportion to that of Sr_2SiO_4, and the specimen heated at 1 360 °C showed the characteristic *X*-ray diffraction pattern of stable $SrSiO_3$.

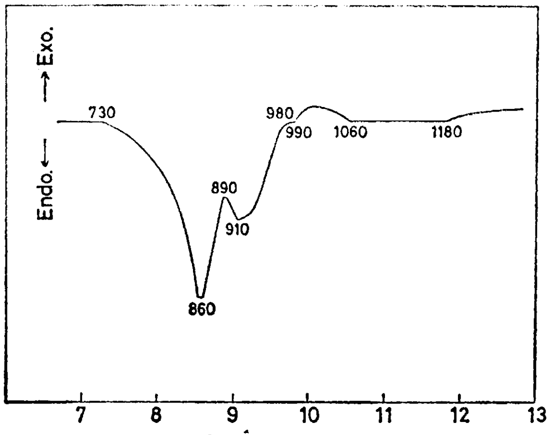

FIGURE 1 D.t.a. curve for the equimolar mixture of $SrCO_3$ and SiO_2. Sample weight, 115 mg

Reaction Mechanism.—It is important to consider two processes for the formation of stable $SrSiO_3$: (*a*) the transformation of metastable $SrSiO_3$, and (*b*) the reaction between Sr_2SiO_4 and SiO_2. Figure 2 shows the results of an *X*-ray diffraction analysis of the specimens quenched after heating for various reaction times at 970 °C using the starting powder A. The amounts of Sr_2SiO_4, metastable $SrSiO_3$, and stable $SrSiO_3$ were determined from the heights of the characteristic peaks at $d = 2.80$ Å,[7] $d = 2.68$ Å,[4,5] and $d = 3.57$ Å,[6] respectively, in comparison with those of the well formed specimens obtained by heating the same powder at 980 °C (1 h) for Sr_2SiO_4, 910 °C (1 h) for metastable $SrSiO_3$, and 1 360 °C (30 min) for stable $SrSiO_3$. The amount of Sr_2SiO_4 increased with time regardless of formation of $SrSiO_3$. From this result, it can be considered that Sr_2SiO_4 was directly formed by the reaction between $SrCO_3$ and SiO_2, not from $SrSiO_3$ and $SrCO_3$. Metastable $SrSiO_3$, after attaining a constant value in a short time, was immediately transformed into stable $SrSiO_3$. The fraction of stable $SrSiO_3$ transformed was $33.3 \pm 0.2\%$. On the other hand, reaction isotherms above 1 180 °C showed that the fraction of $66.7 \pm 0.02\%$ stable $SrSiO_3$ is formed by the reaction of SiO_2 with Sr_2SiO_4 (Figure 3). From the above mentioned results and the high-temperature *X*-ray analysis data, the reaction mechanism can be proposed as equations (1)—(4).

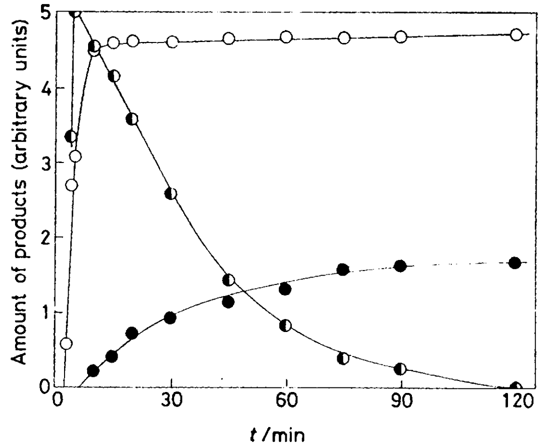

FIGURE 2 Results of *X*-ray diffraction analysis during the reaction at 970 °C. Phases: ○, Sr_2SiO_4; ◐, metastable $SrSiO_3$; ●, stable $SrSiO_3$

$$2\,SrCO_3 + SiO_2 \longrightarrow Sr_2SiO_4 + 2CO_2 \quad (1)$$

$$SrCO_3 + SiO_2 \longrightarrow SrSiO_3\ \text{(metastable)} + CO_2 \quad (2)$$

$$SrSiO_3\ \text{(metastable)} \xrightarrow{\text{transformation}} SrSiO_3\ \text{(stable)} \quad (3)$$

$$Sr_2SiO_4 + SiO_2 \longrightarrow 2\,SrSiO_3\ \text{(stable)} \quad (4)$$

Kinetics of Sr_2SiO_4 *and Metastable* $SrSiO_3$ *Formation.*—The effect of ball-milling on the decomposition of

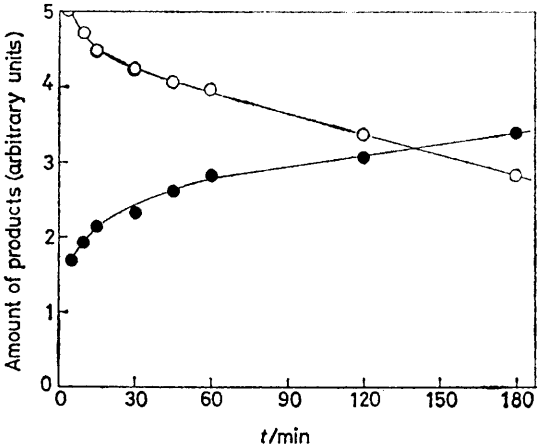

FIGURE 3 Results of *X*-ray diffraction analysis during the reaction at 1 220 °C. Phases: ○, Sr_2SiO_4; ●, stable $SrSiO_3$

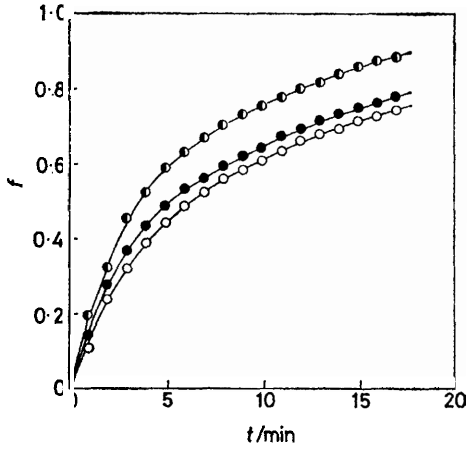

FIGURE 4 Effect of ball-milling on the reaction between $SrCO_3$ and SiO_2 at 770 °C. Ball-milled time: ○, 20; ●, 90; ◐, 190 h. f = Fraction of $SrCO_3$ decomposed in time t (see Figure 5)

$SrCO_3$, reactions (1) and (2), has been studied. Figure 4 shows the curves of f *vs.* time 7 at 770 °C, where f is the fractional decomposition of $SrCO_3$. Apparently, prolonged ball-milling promoted the decomposition of $SrCO_3$. Among the kinetic laws which have been proposed for solid-state reactions, the best fit is obtained with the equation for diffusion-controlled reaction derived by Jander[8] as shown in Figure 5. The rate constants at various temperatures were determined from the slopes of the straight lines. Arrhenius plots yielded the apparent activation energy of 215.5 kJ mol^{-1} irrespective of the ball-milling time (Figure 6). From the results it was found that the ball-milling increases only the frequency factor without changing the reaction mechanism. The increase in the reactivity caused by ball-milling was also detected in d.t.a.; two successive endothermic peaks corresponding to the formation of Sr_2SiO_4 and metastable $SrSiO_3$ in the starting powders B and C were observed for lower temperatures, at about 5 and 15 °C, respectively, in comparison with those of the starting powder A.

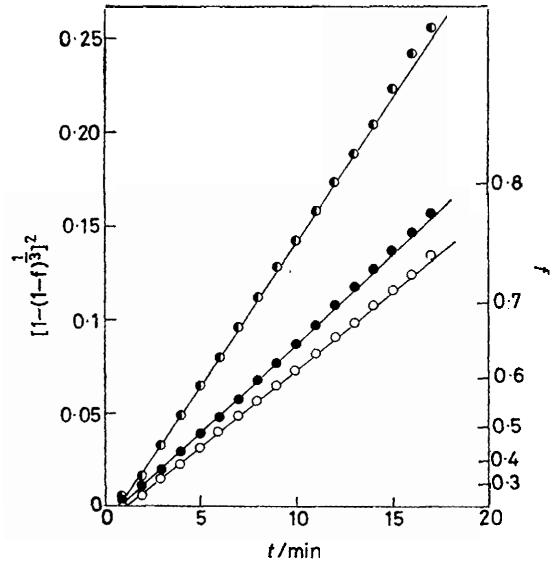

FIGURE 5 Plots of $[1 - (1 - f)^{\frac{1}{3}}]^2$ *vs.* time, t, of the data shown in Figure 4. Ball-milled time: ○, 20; ●, 90; ◐, 190 h

Electron micrographs of starting powders are shown in Figure 7. The SiO_2 particles of the starting powders A and B are contained in a state of aggregation. On the other hand, SiO_2 particles dispersed over the whole surface of $SrCO_3$ were observed in the starting powder C. Therefore, the effect of ball-milling, as in the $BaCO_3$–SiO_2 system,[9] is possibly interpreted in terms of the decrease in particle size of $SrCO_3$ in the early stages and of the improvement of SiO_2 dispersion in the later stages of milling.

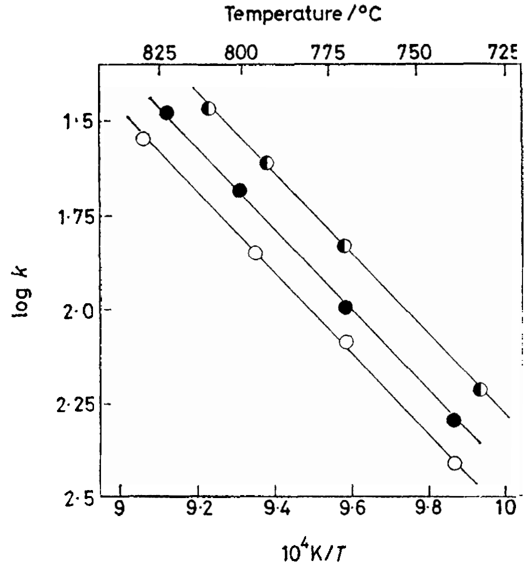

FIGURE 6 Temperature dependences of the rate constants for the decomposition of $SrCO_3$. Ball-milled time: ○, 20; ●, 90; ◐, 190 h

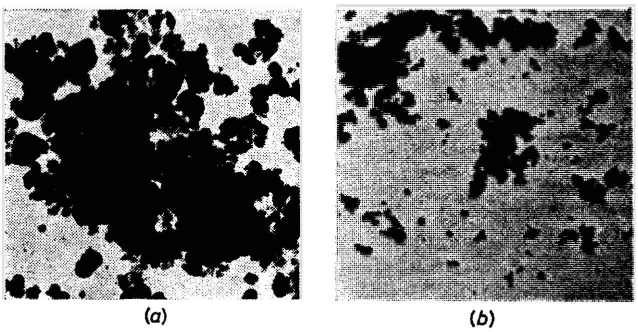
(a) (b)

FIGURE 7 Electron micrographs of starting powders (× 20 000). (*a*) Ball-milled for 20 h, (*b*) ball-milled for 190 h

Kinetics of Stable $SrSiO_3$ *Formation from* Sr_2SiO_4 *and* SiO_2.—The fractional formation of stable $SrSiO_3$ was determined as a function of time at different temperatures. The specimen containing 33.3% stable $SrSiO_3$ obtained by heating the starting powder A for 1 h at

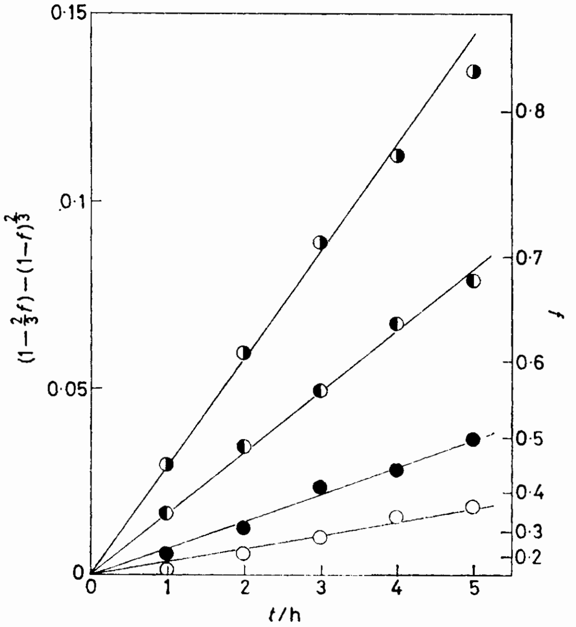

FIGURE 8 Plots of $(1 - \frac{2}{3}f) - (1 - f)^{\frac{2}{3}}$ *vs.* time, *t*. Temperature: ○, 1 220; ●, 1 250; ◐, 1 280; ◑, 1 310 °C. f = Fracture of stable $SrSiO_3$ formed in time t

1 100 °C was used as a starting material. A well formed specimen was heated for 30 min at 1 360 °C. Calcium fluoride (CaF_2) was used as an internal standard. The data can be interpreted in terms of the diffusion-controlled equation of Ginstling and Brounshtein.[10] Figure 8 shows the plots of $(1 - \frac{2}{3} f) - (1 - f)^{\frac{2}{3}}$ against t, where f is the fraction of $SrSiO_3$ formed in time t. An Arrhenius plot of these rate constants gave the activation energy of 510 kJ mol^{-1}.

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REFERENCES

[1] W. Jander and J. Wuhrer, *Z. Anorg. Allg. Chem.*, 1936, **226**, 225.
[2] V. B. Glushkova and E. K. Keler, *Zh. Prikl. Khim.*, 1957, **30**, 517.
[3] E. T. Carson and L. S. Wells, *J. Res. Nat. Bur. Stand.*, 1953, **51**, 73.
[4] T. Takahashi and R. Roy, *J. Am. Ceram. Soc.*, 1975, **58**, 348.
[5] O. Yamaguchi, K. Matumoto, and K. Shimizu, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 237.
[6] *X*-Ray powder diffraction data file (ASTM card 6-0415).
[7] *X*-Ray powder diffraction data file (ASTM card 18-1281).
[8] W. Jander, *Z. Anorg. Allg. Chem.*, 1927, **163**, 1.
[9] T. Yamaguchi, K. Matumura, and K. Kuno, *Nippon Kagaku Kaishi*, 1974, 17.
[10] A. M. Ginstling and B. I. Brounshtein, *Zh. Prikl. Khim.*, 1950, **23**, 1249.