Thermochimica Acta, 95 (1985) 201–211
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF ALKALINE EARTH METAL DOPANTS ON THE THERMAL DECOMPOSITION OF THE $CaCO_3$–SiO_2 SYSTEM.
PART II. FORMATION OF DICALCIUM SILICATE

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(Received 21 May 1985)

ABSTRACT

Mixtures of calcium oxide (taken as carbonate) and silica in 2:1 molar ratio containing varying amounts of MgO, $SrCO_3$ and $BaCO_3$ as dopants were subjected to thermal treatment up to 1450°C. The exothermic peaks at 1200°C and above (beyond the decomposition temperature of calcium carbonate) have been examined to elucidate the phases formed. The exothermic peak at 1210°C without dopant was found to conform to the β-dicalcium silicate phase with a significant amount of free lime and cristobalite along with small amounts of the γ-C_2S phase. MgO at 0.1–1% leads to the formation of β- and γ-dicalcium silicate phases at 1420–1430°C, while 5% MgO results in the formation of the β-C_2S phase at 1360°C. $SrCO_3$, in the concentration range studied, leads to the stabilization of β-C_2S, but does not lower its temperature of formation. $BaCO_3$ at 0.1–1% assists in the formation of the β-dicalcium silicate phase, but 5% BaO forms a mixture of β- and α'_H-C_2S phases at a lower temperature.

INTRODUCTION

The effects of alkaline earth metal dopants on the thermal decomposition of the $CaCO_3$–SiO_2 system has been reported earlier in Part I [1]. The decomposition is complete below 910°C. The dopants not only influence the exotherms, indicating the formation of the dicalcium silicate phase, but also give rise to various polymorphs, α, α', β and γ, of the dicalcium silicate phase. These polymorphs constitute the hydraulic C_2S phase which is a combination of β- and α'-C_2S phases [2]. The monoclinic β form is reported to be stabilized by some additives, such as B_2O_3, Na_2O, K_2O, BaO and Cr_2O_3 [3–6].

Since alkaline earth oxides, MgO, SrO and BaO, occur as associated minerals in the raw materials used for cement manufacture, it is important to

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0040-6031/85/$03.30

investigate their role in the formation of dicalcium silicate using $CaCO_3$ (G.R.) and quartz powder as starting materials. The other precursors reported for making dicalcium silicate are pure $Ca(OH)_2$ and silicic acid [7], $CaCO_3$ and silica gel [8], and ethyl orthosilicate hydrolysed by a solution of $Ca(NO_3)_2$ [9].

In the present communication, the effects of varying amounts of MgO, Sr CO_3 and $BaCO_3$ on the temperature of formation of the dicalcium silicate phase and the other intermediate phases during thermal treatment up to 1450°C are reported.

EXPERIMENTAL

The reagents used, the method of preparation of the starting materials, and the instrument used for thermal analysis have been discussed in an earlier paper [1]. Dried, powdered samples (60 mg), passed through a 100-μm sieve, were heated at a rate of 8°C min^{-1} in a platinum crucible to temperatures up to 1450°C. The exothermic peaks for the formation of dicalcium silicates have been recorded. The powdered starting materials were heated at the same rate in a quench furnace to the temperature where the exothermic peak ends and after 30 min the samples were quenched in liquid nitrogen to arrest the reaction. The X-ray diffraction studies of the quenched samples were made with a Philips X-ray diffractometer (PW 1120) for identification of the phases formed. Samples for X-ray diffraction studies were prepared by passing the powdered material through a 45-μm sieve and then pressing it into a sample holder. X-ray diffraction patterns, using a CuK_α target and nickel filter, have been taken for dicalcium silicate and dicalcium silicate doped with alkaline earth oxides.

RESULTS AND DISCUSSION

The thermal curve of the $2CaCO_3$–SiO_2 system gives two exothermic peaks at 1210 and at 1425°C after the decomposition of $CaCO_3$ (Figs. 1–3). X-ray diffraction studies of the sample ($2CaCO_3$–SiO_2) indicate that, under the reaction conditions the β-dicalcium silicate phase is formed at 1210°C. Additional peaks (d values (Å): 2.77, 2.40, 1.70, 1.45) indicate the presence of excess free CaO leading to the conclusion that the reaction does not go to completion at this temperature. The cristobalite phase is also discernible by XRD (d values (Å): 4.05, 2.84, 2.485) indicating incomplete reaction. A small quantity of the γ-C_2S phase is also present, as characterized by XRD peaks. Table 1 shows that the observed d values closely match those reported in the literature.

X-ray diffraction studies of the sample obtained by quenching in liquid nitrogen at 1425°C reveal the presence of a significant quantity of both β-

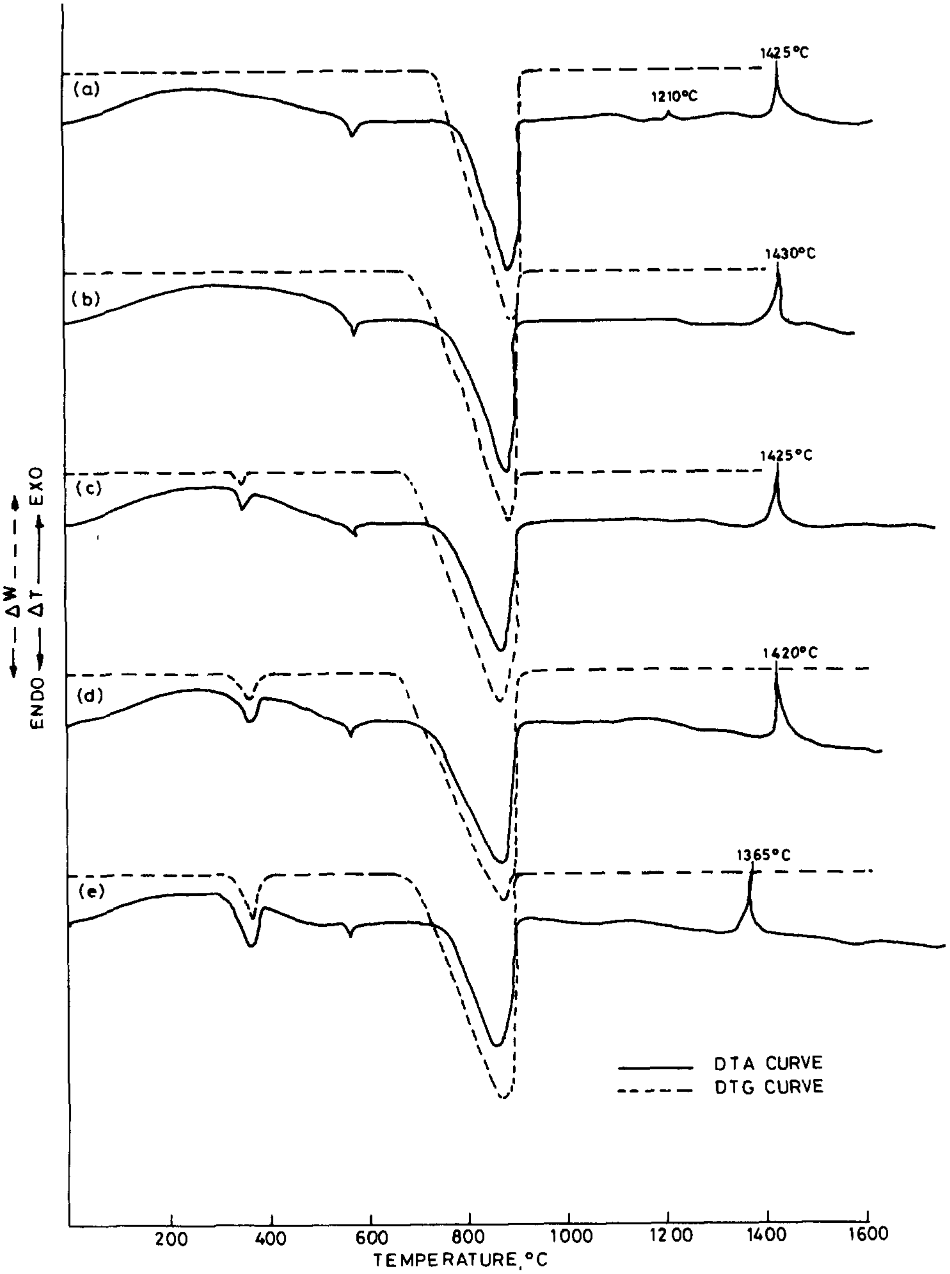

Fig. 1. Thermal curves of (a) $2CaCO_3$-SiO_2, (b) $2CaCO_3$-SiO_2 + 0.1% MgO, (c) $2CaCO_3$-SiO_2 + 0.5% MgO, (d) $2CaCO_3$-SiO_2 + 1% MgO, (e) $2CaCO_3$-SiO_2 + 5% MgO.

and γ-C_2S phases. There is a near absence of free lime indicating that the reaction is complete. X-ray diffraction studies on the samples obtained by repeated firing (4–5 times) of the reacting mixtures at 1425°C indicate that the phase present is β-C_2S. It may be concluded from the above investiga-

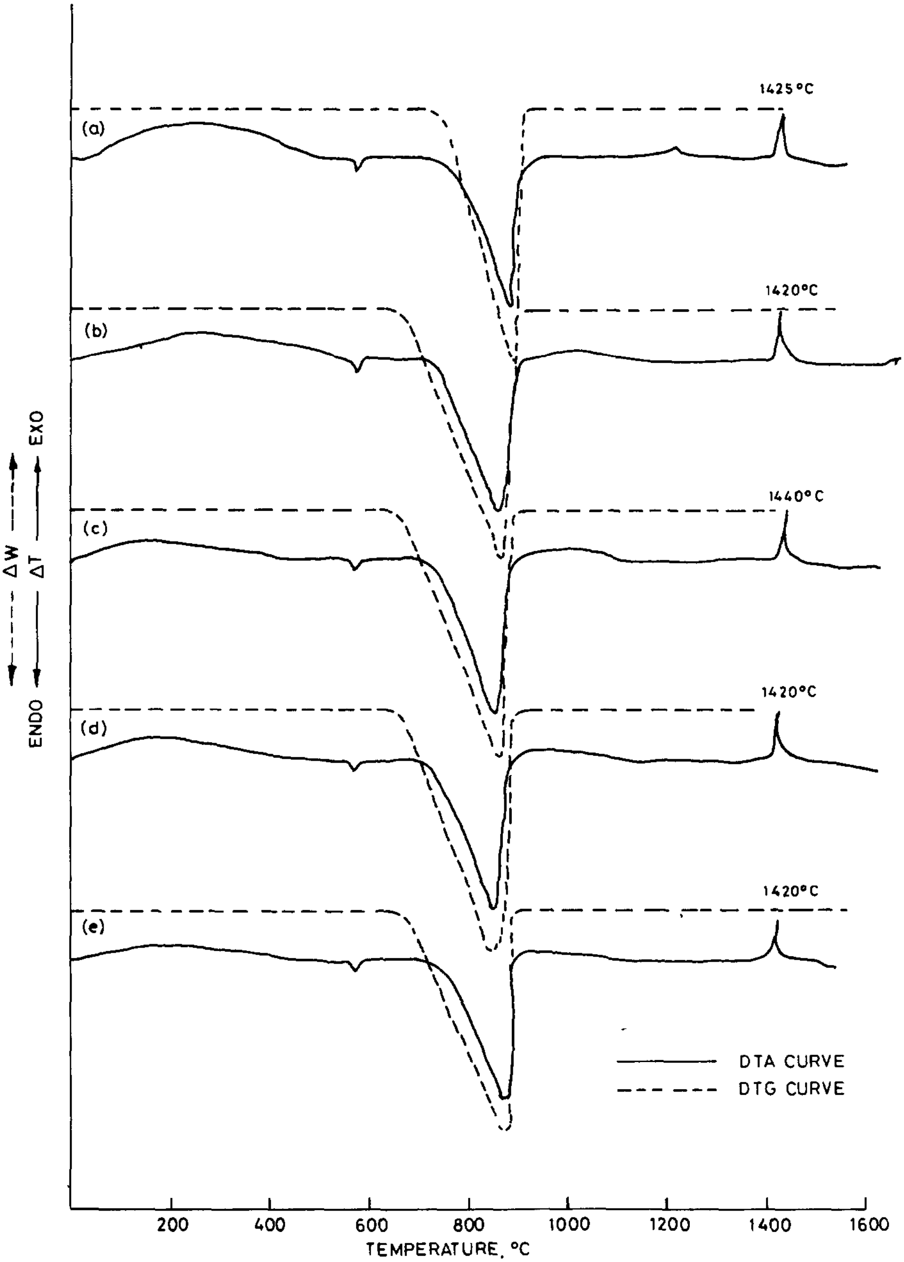

Fig. 2. Thermal curves of (a) $2CaCO_3$-SiO_2, (b) $2CaCO_3$-SiO_2 + 0.1% $SrCO_3$, (c) $2CaCO_3$-SiO_2 + 0.5% $SrCO_3$, (d) $2CaCO_3$-SiO_2 + 1% $SrCO_3$, (e) $2CaCO_3$-SiO_2 + 5% $SrCO_3$.

tions that at lower temperatures, the formation of β-C_2S takes place due to its stabilization by free lime and, since the reaction mixture becomes low in free CaO, a mixture of β- and γ-C_2S phases is obtained. The mixture, on prolonged heat-treatment, can result in the stabilization of β-C_2S. These

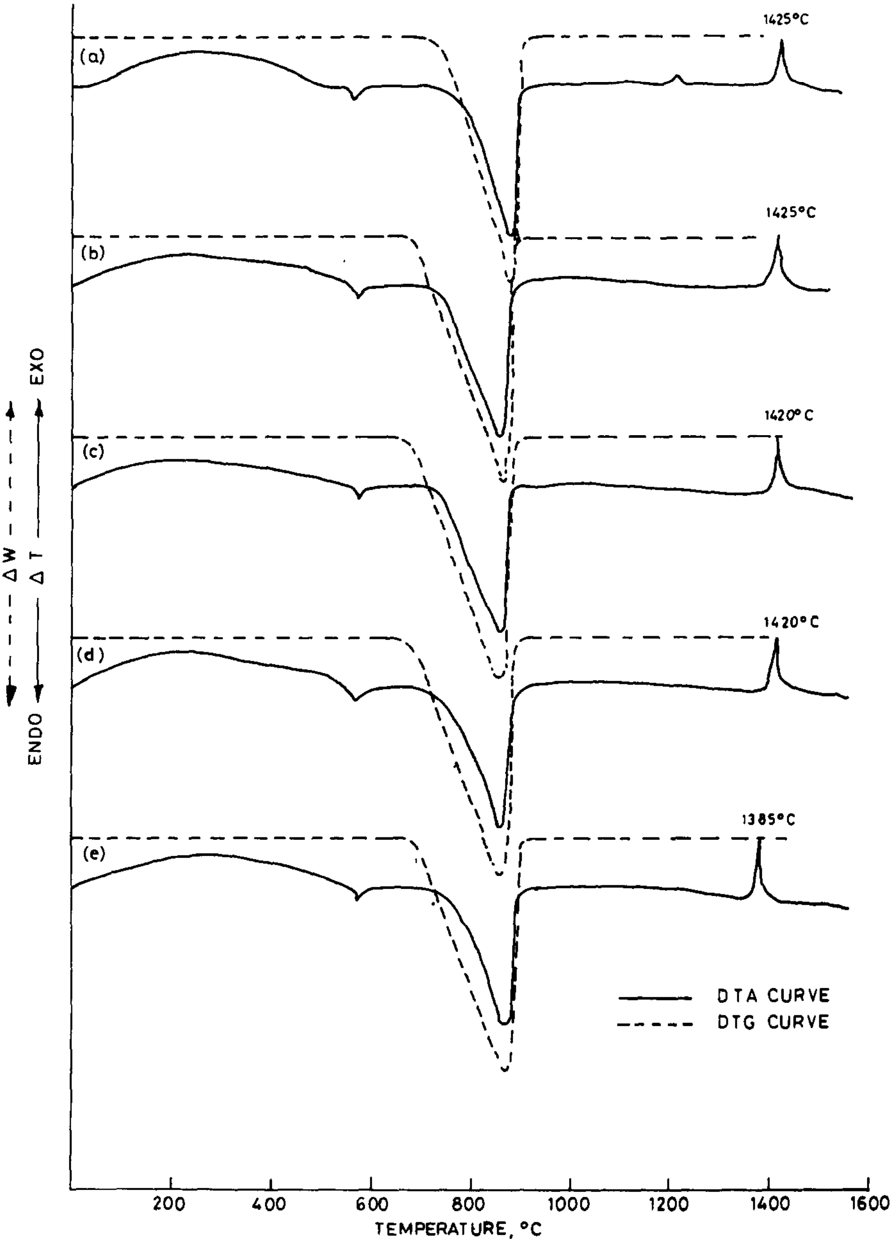

Fig. 3. Thermal curves of (a) $2CaCO_3$-SiO_2, (b) $2CaCO_3$-SiO_2 + 0.1% $BaCO_3$, (c) $2CaCO_3$-SiO_2 + 0.5% $BaCO_3$, (d) $2CaCO_3$-SiO_2 + 1% $BaCO_3$, (e) $2CaCO_3$-SiO_2 + 5% $BaCO_3$.

studies are supported by the works of Korneev and Bygalina [10].

Differential thermal analyses of the 2-$CaCO_3$–SiO_2 system doped with 0.1, 0.5, 1.0 and 5.0% MgO were carried out (Fig. 1). The results are presented in Table 2. The presence of MgO results in a disappearance of the

TABLE 1

Thermal studies of the $2CaCO_3$–SiO_2 system and formation of different phases

Exotherm as shown by DTA (°C)	Experimental conditions	Constituents formed as discernible by XRD	Corresponding most intense *d* values (Å)	*d* values (Å) reported in the literature
1210	reacting mixtures fired to this temperature for 30 min, quenched in liquid nitrogen	Free lime	2.77, 2.40, 1.70. 1.45	2.778, 2.405, 1.70, 1.45
		β-C_2S	2.80, 2.74, 2.77, 2.61	2.80, 2.74, 2.78, 2.608
		cristobalite	4.05, 2.84, 2.485	4.05, 2.84, 2.485
		small amount of γ-C_2S	4.30, 4.04, 3.81, 301, 2.73	4.32, 4.05, 3.81, 3.01, 2.73
1425		β-C_2S	2.80, 2.73, 2.76, 2.61	2.80, 2.74, 2.78, 2.61
		γ-C_2S	4.31, 2.80, 2.485, 2.73	4.32, 2.80, 2.485, 2.73
		small amount of free lime	2.77 2.40, 1.70, 1.45	2.778, 2.405, 1.701 1.45
1425	Reacting mixture fired 3–4 times in furnace, air-quenched	β-C_2S	2.74, 2.77, 2.61	2.74, 2.78, 2.608

TABLE 2

Thermal studies of the $2CaCO_3$–SiO_2 system in the presence of different concentrations of MgO and the formation of different phases

Concentration of MgO (%)	Exotherm as shown by DTA (°C)	Experimental conditions	Constituents formed as discernible by XRD	Corresponding most intense *d* values (Å)	*d* values (Å) reported in the literature
0.1	1430	Reacting mixture fired to the temperature at which the peak ends for 30 min, quenched in liquid nitrogen	γ-C_2S	4.30, 4.05, 3.81, 3.01, 2.73	4.32, 4.06, 3.82, 3.01, 2.73
			β-C_2S	2.74, 2.78 2.61	2.74, 2.78 2.608
0.5	1425				
1.0	1420				
5.0	1360		β-C_2S phase with very little γ-C_2S and MgO (periclase)	2.73, 2.78, 2.61 2, 10, 2.43 1.489, 1.26	2.74, 2.78, 1.49, 2.608 2, 106, 2.43, 1.27

TABLE 3

Thermal studies of the $2CaCO_3-SiO_2$ system in the presence of different concentrations of $SrCO_3$ and the formation of different phases

Concentration of $SrCO_3$ (%)	Exotherm as shown by DTA (°C)	Experimental conditions	Constituents formed as discernible by XRD	Corresponding most intense d values (Å)	d values (Å) reported in the literature
0.1	1420	Reacting mixtures fired to the temperature where the peak ends and quenched in liquid nitrogen	β-C_2S (most intense)	2.74, 2.78, 2.61	2.74, 2.78, 2.608
0.5	1440		γ-C_2S (small amount)	4.30, 4.05, 3.81, 3.01, 2.73	4.32, 4.06, 3.81, 3.01, 2.73
1.0	1420			2.74, 2.78, 2.61	2.74, 2.78, 2.608
5.0	1420		(γC_2S absent) Presence of a small quantity of α'_H-C_2S along with a small quantity of $SrSiO_3$	2.92, 2.763, 3.21, 2.31 2.91, 2.07, 3.57	2.924, 2.763 3.21, 2.33 2.92, 2.07, 3.57

TABLE 4

Thermal studies of the $2CaCO_3$–SiO_2 system in the presence of different concentrations of $BaCO_3$ and the formation of different phases

Concentration of $BaCO_3$ (%)	Exotherm as shown by DTA (°C)	Experimental conditions	Constituents formed as discernible by XRD	Corresponding most intense *d* values (Å)	*d* values (Å) reported in the literature
0.1	1425	Reacting mixtures fired to the temperature (where the peak ends) for 30 minutes and quenched in liquid nitrogen	β-C_2S	2.80, 2.74, 2.78, 2.61, 2.19	2.80, 2.74, 2.78, 2.608, 2.19
0.5	1420		β-C_2S with small quantities of γ-C_2S	2.80, 2.78, 2.74, 2.61, 2.19	2.80, 2.78, 2.74, 2.608, 2.19
1.0	1420		β-C_2S with a appreciable amount of γ-C_2S	2.74, 2.78, 2.80, 2.61, 2.19, 3.00	2.74, 2.78, 2.795, 2.608, 2.19, 3.01
5.0	1385		β-C_2S with a small quantity of α'_H-C_2S	2.74, 2.78, 2.72, 2.92, 2.80	2.74, 2.778, 2.721, 2.919, 2.80

exothermic peak at 1210°C, which was observed in the system without dopant. However, an exothermic peak was observed in the range 1420–1430°C with 0.1–1% MgO, indicating that the addition of MgO up to 1% does not lower the temperature of formation of dicalcium silicate. However, the addition of 5% MgO significantly lowers the temperature of formation of β-C_2S, with its formation at 1365°C. X-ray diffraction investigations on the magnesium-doped samples heated to temperatures at which the exothermic peak ends for 30 min, and quenched in liquid nitrogen, are presented in Table 2. It is evident that with up to 1% MgO, both β- and γ-C_2S phases are formed, and with 5% MgO, β–C_2S is formed along with free MgO. This study was also confirmed by Boigalina [11].

Similar experiments were carried out using $SrCO_3$ and $BaCO_3$ as dopants. DTA exotherms are given in Figs. 2 and 3. The DTA studies indicate that $SrCO_3$ does not lower the temperature of formation of the dicalcium silicate phase, and the exothermic peaks of C_2S formation are obtained at 1420–1440°C at all concentrations of $SrCO_3$. Starting materials ($2CaCO_3$–SiO_2) with all the concentrations of $SrCO_3$ used (0.1–1%), fired up to the above temperature for $\frac{1}{2}$ h, and quenched in liquid nitrogen, show that the β-dicalcium silicate phase is formed at these temperatures. A higher percentage of $SrCO_3$ (5%) results in the formation of small amounts of α'_H-C_2S and Sr_2SiO_4 along with β-C_2S. Similarly, $BaCO_3$ (0.1–1%) does not lower the temperature of formation of the β-dicalcium silicate phase, whereas 5% $BaCO_3$ lowers the temperature of formation to 1385°C, and forms a combination of α'_H- and β-dicalcium silicate phases.

CONCLUSION

These dopants hasten the formation of dicalcium silicate in comparison to the pure precursors, since there repeated firing is required. Dopants at a 0.1–1% concentration do not affect the reaction temperature significantly. However, 5% magnesium oxide or barium carbonate significantly lowers the temperature of formation of dicalcium silicate phase, but 5% strontium carbonate does not lower it.

AKNOWLEDGEMENT

The authors are thankful to Dr. H.C. Visvesvaraya, Chairman and Director General, National Council for Cement and Building Materials, New Delhi, for providing research facilities in pursuing Ph.D. studies to one of the authors (V.K.M.).

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