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STUDIES OF CALCIUM ORTHOSILICATE POLYMORPHISM BY DIFFERENTIAL THERMAL ANALYSIS

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The polymorphic transitions of calcium orthosilicate have been studied by means of differential thermal analysis. The parameters of β-Ca_2SiO_4 synthesis without stabilizers have been established.

The similarity of the crystal structures of calcium orthosilicate and alite, the analogous hydration mechanisms and the relatively low temperature of Ca_2SiO_4 synthesis are the reasons for the investigation of binders containing Ca_2SiO_4 as a main component. β-Ca_2SiO_4 is the polymorph with the best hydraulic properties. This phase is metastable in the whole temperature range and can be stabilized by the addition of certain impurities, viz. B^{3+}, P^{5+}, Cr^{6+} or As^{3+}. Pritts and Daugherty [1] proved that these stabilizers lower the rate of Ca_2SiO_4 reaction with water.

The aim of this work was to determine the parameters of β-Ca_2SiO_4 synthesis without the utilization of stabilizers. The γ-Ca_2SiO_4 of high purity produced during the long-lasting heating at 1500° of a mixture of $CaCO_3$ + silica gel was used as starting material. The γ-Ca_2SiO_4 phase forms characteristic aggregates of thin needles and plates covered with a network of cracks.

The DTA studies were carried out using a Setaram thermoanalyser and revealed, during heating and cooling, all the peaks corresponding to Ca_2SiO_4 polymorphic transitions as described by Niesel and Thormann [2]. The occurrence of the α'_m polymorph has not been confirmed [3]. Further examination by DTA, XRD and high-temperature microscopy showed the influence of the thermal treatment temperature and the rate of cooling on the rate of the polymorphic transition $\beta \rightarrow \gamma$-Ca_2SiO_4, as well as on the phase composition of the sample. It was clearly seen in the DTA curves that lowering of the heating temperature reduced the $\beta \rightarrow \gamma$ transition peak area and altered the peak profile. The samples heated at 1450° gave only the γ-Ca_2SiO_4 phase after subsequent cooling. Lowering of the heating temperature to 1400° resulted in a 17% β phase content after cooling. Samples

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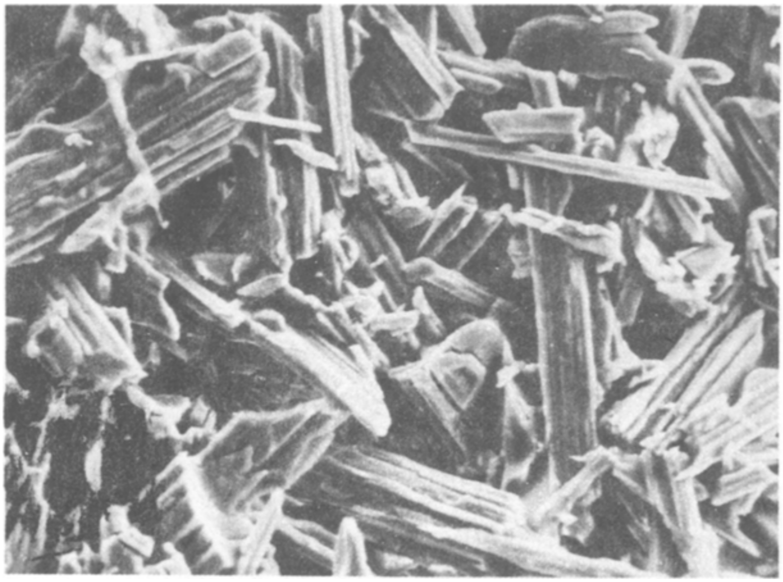

Fig. 1 SEM micrograph of γ-Ca_2SiO_4 sample. Magnification 500 ×

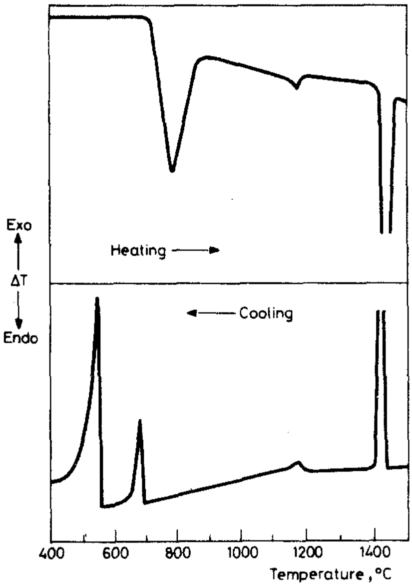

Fig. 2 DTA curve of Ca_2SiO_4 sample heated at 1500 °C. Heating: 795 C, 1184 °C, 1443 °C. Cooling: 1442 °C, 1180 °C, 680 °C, 552 °C

heated at lower temperatures contained larger amounts of β phase: at 1300° 25%, at 1200° 40%, at 1000° 60%, and at 500° 65% β-Ca_2SiO_4, respectively. A further β-Ca_2SiO_4 content increase was produced by repeated "heating-cooling", unless the transition temperature $\alpha'_H \rightarrow \alpha$ was exceeded,

The shrinkage of the Ca_2SiO_4 sinter relates strongly to the phase composition changes. Small changes in the linear dimensions emerge as early as at 950°. Rapid shrinkage takes place at 1420–1450°. The acceleration of the sintering process at 1420–1450° results from the $\alpha'_H \rightarrow \alpha$ transition.

The $\beta \rightarrow \gamma$ transition is influenced by the starting material graining. The samples prepared from γ-Ca_2SiO_4 composed of grains less than 2 μm and heated at 1300° for 2 hours gave, after cooling, only the β-Ca_2SiO_4-containing product. The destruction of Ca_2SiO_4 aggregates makes the sintering and recrystallization difficult. In the small crystals formed during cooling, the probability of γ phase nucleation is very low, and this fact determines the β phase stabilization. When the γ-Ca_2SiO_4 aggregates are not disintegrated mechanically or by repeated "heating-cooling", the sintering and recrystallization can occur easily. These processes are favoured by the large contact surface of the Ca_2SiO_4 fibres and their compatible orientation. The crystal growth is then sufficient to ensure γ phase formation during cooling. When Ca_2SiO_4 is heated above the temperature of $\alpha'_H \rightarrow \alpha$ polymorphic transition, the sintering process takes place in larger areas than the adjacent fibres in particular aggregates. The large crystals then form in spite of the primary fine graining, and the $\beta \rightarrow \gamma$-Ca_2SiO_4 transition occurs on cooling.

The rapid cooling of samples in the range of the $\alpha \rightarrow \alpha'_H$ transition is another means of β-Ca_2SiO_4 stabilization as a consequence of very fine-grained α'_H phase formation. Rapid cooling from a temperature lower than 1420° does not ensure the pure β-Ca_2SiO_4 phae preparation. A mixture of β and γ phases can thus be obtained, with the β/γ ratio depending on the heating temperature and cooling rate.

References

1 J. M. Pritts and K. E. Daugherty, Cem. Concr. Res., 6 (1976) 783.

2 K. Niesel and P. Thormann, Tonind. Ztg., 91 (1967) 362.

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Zusammenfassung — Mittels DTA wurden die Polymorphieübergänge von Kalziumorthosilikat untersucht. Die Parameter zur Synthese von β-Ca_2SiO_4 ohne Stabilisatoren wurden bestimmt.

Резюме — Методом ДТА изучены полиморфные переходы орто-силиката кальция. Установлены условия синтеза β-Ca_2SiO_4 без стабилизирующих добавок.