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DIFFERENTIAL THERMAL ANALYSIS OF THE PHASE TRANSITION OF DICALCIUM ORTHOSILICATE Ca_2SiO_4 UNDER A REDUCING ATMOSPHERE

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The $\beta \rightarrow \gamma$ transformation of Ca_2SiO_4 was investigated with regard to the disintegration of the sinter in alumina manufacturing. DTA was applied to study the effect of the reducing atmosphere upon the course of the polymorphic transitions of Ca_2SiO_4, and particularly the self-disintegration process. Pure synthetic dicalcium orthosilicate and blends of pure components from the system $CaO–Al_2O_3–SiO_2–Fe_2O_3$ were compared with technological mixtures of limestone and fly ash. Data obtained from the DTA runs allowed the specification of technical parameter for both firing and cooling of the sinter.

Dicalcium orthosilicate (C_2S) is an important component of self-disintegrating sinter, an intermediate in the manufacturing of alumina by the Crzymek method [1]. This method includes the disintegration of a sinter due to the polymorphic transition of β-Ca_2SiO_4 into its γ modification under certain thermodynamic conditions.

C_2S is reported to occur in five polymorphic modifications (α, α'_H, α'_L β and γ), differing from one another both in space symmetry and in cell parameters. They have been widely described in the literature [2–5], and were reviewed recently by Guinier and Regourd [6]. A scheme of the transformations between the C_2S modifications (after [7]) is presented in Fig. 1.

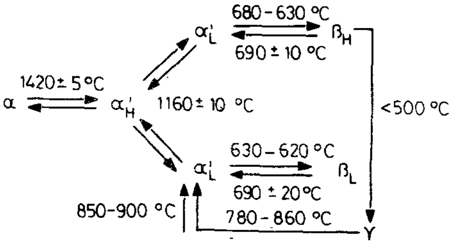

Fig. 1 Polymorphic transitions of dicalcium orthosilicate, Ca_2SiO_4, according to K. Niesel and P. Thormann [7]

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The course of the $\beta \rightarrow \gamma$ transition determines the properties of the quenched sinter and has a strong effect on the size of the very fine solids produced in the disintegration process.

However, the sate of this process is conditioned by several factors. The most important are the way in which the thermal treatment is performed and the nature of the admixtures incorporated into the system. Some admixtures even in trace quantities, may increase the stability of the β-phase. A considerable stabilizing effect is produced by species such as As^{5+}, P^{5+}, B^{3+}, V^{5+} and Cr^{6+}. This can be avoided when C_2S is synthesized under a reducing atmosphere [8].

DTA has been used in many studies dealing with the polymorphism within the series of C_2S modifications. It has provided a large set of data concerning the temperature intervals of phase transitions, quantitative lattice energy alterations relating to the processes, and the physico-chemical nature of the phenomenon of self-disintegration due to the conversion of β-C_2S into its γ form.

In the present study, the DTA technique was applied to determine the effect of the reducing oven atmosphere upon the synthesis and mechanism of polymorphic transitions of C_2S from both well-defined and technical raw materials.

Special attention was paid to the quenching process of the fired sinter with regard to the reducing atmosphere in the kiln.

Experimental

Mixtures tested in this study were as follows:

1. $CaCO_3$ (precipitated) and colloidal silica—designed for the synthesise of pure C_2S.
2. $CaCO_3$ (precipitated), colloidal silica, Al_2O_3 and Fe_2O_3—designed for the preparation of a sinter consisting of C_2S and a calcium aluminate phase of general formula $Ca_{12}Al_{14}O_{33}$ within the system $CaO–Al_2O_3–SiO_2–Fe_2O_3$.
3. Raw materials used in technology: limestone and lignite fly ash—designed for the preparation of a "technological" sinter.

DTA tests were performed with a TA-1 Mettler thermoanalyser.

All mixtures were heated at a constant rate of 10 deg min^{-1} until the assumed sintering temperature was reached. This was maintained for 1 h, and the sample was then cooled at a rate of 10 deg min^{-1} down to 20°.

Firing was performed in a high-temperature laboratory oven provided with an analytical and recording system suitable for the analysis of CO, CO_2 and O_2.

The reducing atmosphere was achieved through the burning of graphite; it contained approximately 10% of CO.

The gas flow rate was kept constant at 10 l h^{-1}.

Results and discussion

DTA data collected during heating and cooling of the reagent mix designed for the synthesis of C_2S are shown in Figs 2 and 3. It follows from the heating curve (Fig. 2) that the decomposition of $CaCO_3$ in air begins at 810°, passes through a maximum at 920°, and is complete at 975°. The corresponding decomposition temperatures of $CaCO_3$ in an atmosphere of CO are 815, 905 and 950°, respectively.

The effect of the oven atmosphere on the sintering process and reactions between oxides is usually explained in terms of the adsorption of gases on the surface of the reagent grains. This results in alterations in the dissociation of the mix components and increases the reactivities of the combining oxide species.

The endothermic effect at 1430° is assigned to the $\alpha'_H \to \alpha$ transition of C_2S. Fierens and Picquet [9] claim that, due to this process, the Hedvall's reaction rate is increased by Hedvall's effect. C_2S reacts very rapidly with silica, producing silicates

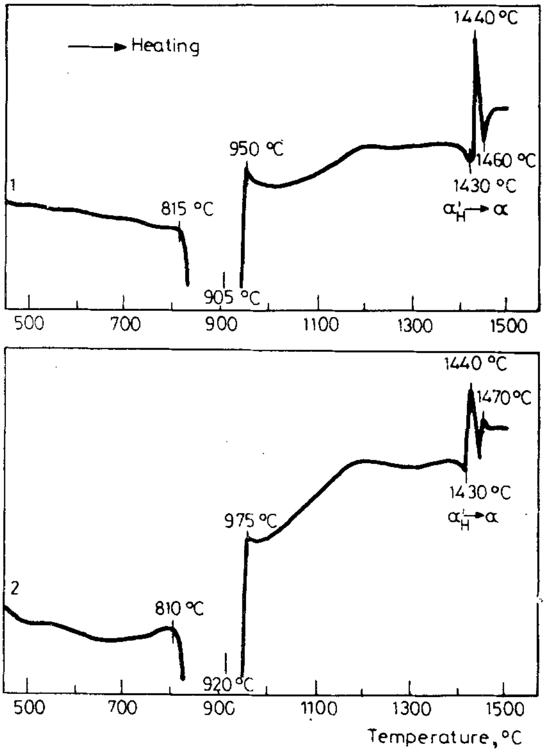

Fig. 2 DTA curves of mix designed to synthesize Ca_2SiO_4 fired up to 1500 °C: 1 – in the CO atmosphere, 2 – in air

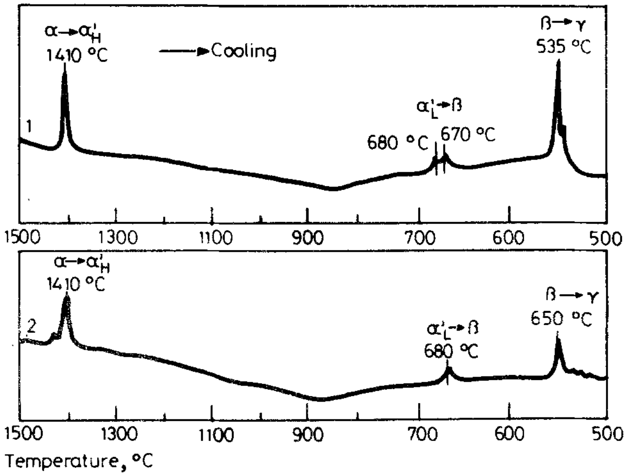

Fig. 3 DTA cooling curves of mix designed to synthesize Ca_2SiO_4 fired up to 1500 °C and maintained in that temperature for 1 hour: 1 – in the CO atmosphere, 2 – in air

of lower basicity, predominantly $Ca_3Si_2O_7$ [9]. This reaction is related to the exothermic effect at 1440°.

According to the thermodynamic properties of the binary system $CaO–SiO_2$, at 1443° the melting of low basic silicates takes place. The liquid phase immediately reacts with free lime to produce C_2S. The exothermic effect at 1470° may be accounted for by this process.

As can be seen in Fig. 2, the character of the DTA curves in the temperature range of C_2S formation is similar, regardless of the oven atmosphere applied during firing.

On cooling in air, the DTA curves (Fig. 3) reveal two exothermic peaks within the $\alpha \to \alpha'_H$ transformation range.

When a gas containing CO was passed through the oven, the DTA record on cooling showed only one exothermic peak (at 1410°) related to the $\alpha \to \alpha'_H$ transition. No thermal effect corresponding to the $\alpha'_H \to \alpha'_L$ was recorded. It should be emphasize that this transition produces the lowest thermal effect of all the polymorphic conversions of C_2S [10].

At 680°, the DTA curves reveal a thermal effect assigned to the transition $\alpha'_L \to \beta$. However, this effect appears to be split into two peaks at 680 and 670° in records taken in a CO-containing atmosphere.

The exothermic effect of the self-disintegration process due to the transformation $\beta \to \gamma$ in C_2S is found at 550° and 535° for samples sintered in air and CO atmosphere, respectively.

Since the C_2S in industrially manufactured aluminate sinters occurs together with aluminate and ferrite phases, attention was directed towards the system

$CaO-Al_2O_3-SiO_2-Fe_2O_3$. Experiments were performed on this system to study the formation and decomposition of the self-disintegrating sinter in both air and CO oven environments.

DTA curves illustrating the self-disintegration of sinters fired at 1350, 1400 and 1450° are shown in Fig. 4.

Samples fired at 1450° were molten regardless of the oven atmosphere. No thermal effect which could be related to the self-disintegration process was registered in the DTA curves taken during cooling in a CO atmosphere.

In contract, the sample fired in the same way but in air revealed a thermal effect in the DTA curve on cooling, which could be assigned to the transition of β-C_2S into its γ-modification, although the sinter did not disintegrate.

When firing was performed at 1400° in air, thermal effects corresponding to the $\beta \rightarrow \gamma$ transformation of C_2S could be distinguished within the temperature range from 260 to 195° in the cooling part of the DTA curve; the sample was partly decomposed.

When a CO atmosphere was applied, no similar effects were observed.

However, when samples were fired at 1350°, self-disintegration followed both in the process performed in air and in that in a CO-containing atmosphere. Nevertheless, differences were noted in the thermal effects assigned to the C_2S phase transformations.

These results suggest that in a reducing oven atmosphere, the temperature at which the liquid phase appears is lowered due to the presence of Fe^{2+} ions in the

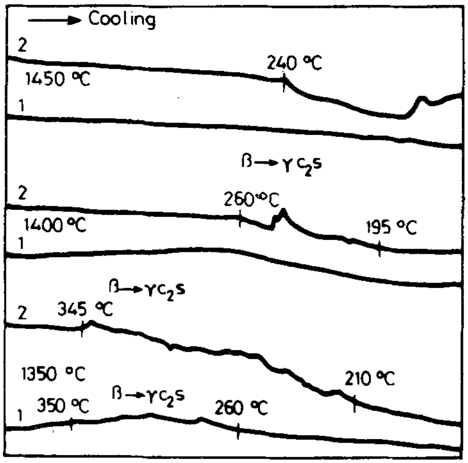

Fig. 4 DTA cooling curve of a sinter produced within the system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ fired up to 1350, 1400, 1450 °C: 1 – in the CO atmosphere, 2 – in air

system. In parallel, the self-disintegration process is diminished, as could be observed in particular at 1450 and 1400°.

Thus, it may be concluded that under these temperature conditions the β-phase becomes stabilized.

DTA records on cooling of a technological sinter synthesized at 1350° from a mix of limestone and lignite fly ash are presented in Fig. 5. The sinter prepared in air disintegrated within the temperature range from 320 to 180°. When sintering was performed in a CO atmosphere, the self-disintegration process was finished at a higher temperature. The CO apparently has a reducing effect upon these mix ingredients, which would normally act as stabilizers of β-C_2S, thereby making them less effective. As a result, the self-disintegration process is completed within a shorter period of time.

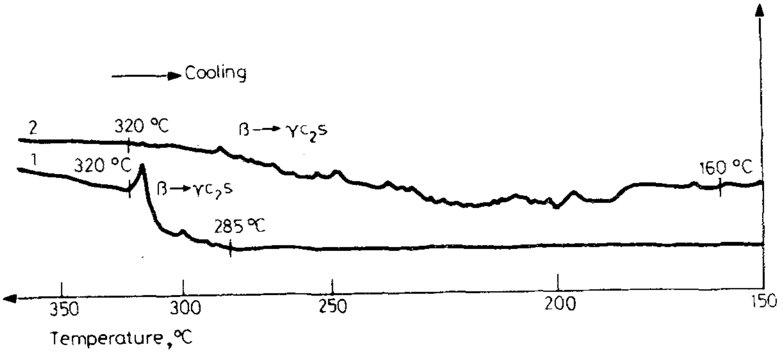

Fig. 5 DTA cooling curves of a sinter prepared from lignite fly ash and limestone at 1350 °C: 1 – in the CO atmosphere, 2 – in air

Conclusions

DTA appeared to be a method adequate for study of the effects of the reducing atmosphere upon the self-disintegration of sinters containing dicalcium orthosilicate.

The CO atmosphere does not essentially affect the $\beta \rightarrow \gamma$ transition of pure C_2S synthesized without any mineral admixtures.

As far as the CaO–Al_2O_3–SiO_2–Fe_2O_3 system is concerned, the effect of the oven atmosphere depends on the firing temperature applied. An excessive amount of the liquid phase produced during sintering at 1400 at 1450° in a CO environment is considered to be the reason for the diminishing of the self-disintegration process.

It has been found advantageous to perform the sintering at 1350° with CO present in the oven atmosphere. It is essential to maintain the reducing conditions during firing, in order to decrease the reactivity of ions stabilizing the β-C_2S phase. This leads to a substantial increase in the yield of the self-disintegration process.

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Zusammenfassung — Die $\beta \rightarrow \gamma$-Umwandlung in Ca_2SiO_4 wurde im Hinblick auf den Zerfall von Sinter in der Tonerdeproduktion untersucht. Mittels DTA wurde der Einfluß einer reduzierenden Atmosphäre auf den Verlauf der polymorphen Umwandlungen von Ca_2SiO_4 und insbesondere auf den Zerrieselungsprozeß verfolgt. Reines synthetisches Ca_2SiO_4 und Gemische reiner Komponenten des Systems CaO–Al_2O_3–SiO_2–Fe_2O_3 wurden mit technischen Mischungen aus Kalk und Flugasche verglichen. Die Ergebnisse von DTA-Versuchen erlauben die Spezifizierung der technischen Bedingungen für das Brennen und Abkühlen des Sinters.

Резюме — Изучено $\beta \rightarrow \gamma$ фазовое превращение ортосиликата кальция относительно раздробления спеков при получении глинозема. Метод ДТА был использован для изучения влияния восстановительной газовой атмосферы на полиморфные превращения ортосиликата кальция и, в особенности, на процесс самораздробления. Чистый синтетический ортосиликат кальция и смеси чистых компонентов в системе CaO–Al_2O_3–SiO_2–Fe_2O_3 были сопоставлены с технологическими смесями известняка и летучей золы. Данные ДТА позволили установить технические параметры нагрева и охлаждения спека.