

SOLID-STATE SYNTHESIS OF PURE BELITE POLYMORPHS

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ABSTRACT. The solid-state synthesis of pure belite polymorphs is still not described in detail. The study of this issue is important for understanding modification transformations, especially between beta and gamma modifications. In this paper, the two-step firing procedure was used to study belite transformations. The first firing step was designed to produce samples with high content of γ -C₂S. These samples were fired again and successfully transformed into β -C₂S without any additional chemicals. In addition to firing parameters, the effect of particle size was also monitored. The experiment succeeded in creating a sample containing 64 % gamma belite in total and also a sample containing a total of 90 % of beta belite.

KEYWORDS: Clinker, belite, polymorphism.

1. INTRODUCTION

Belite, dicalcium silicate, is one of four main minerals in Portland clinker. Belite structure is made of SiO⁴⁻ tetrahedrons connected with calcium ions [1]. Nowadays, five polymorphs of belite are known, which are referred to as α , α' H, α' L, β and γ . Except for gamma modification all of these polymorphs are stable only at high temperatures, but it is possible to stabilize high-temperature polymorphs with suitable cooling method or incorporation of other ions [2]. Successful chemical stabilization was studied and described by many authors. For example, Kim [3] described that addition of B³⁺ ions have positive effect to β -C₂S stabilization. Also, physical stabilization was studied and Chan [4] claims that only particles over 10 μ m can change its modification in order of α' L \rightarrow β \rightarrow γ during cooling. On the other hand, stabilization of different belite polymorphs by solid-state method with no additives is not described in detail.

β -C₂S exhibits a low rate of hydration in Portland cement and its strength is gained mainly after longer hydration time [5]. A more intense increase in strength can be achieved by controlled carbonation during hydration, both for the polymorphic beta modification and also for the gamma modification, which is non-reactive under classic hydration conditions. The effect of incorporating CO₂ back into the structure of the mineral, in combination with the lower required firing temperature, is an interesting option for reducing the carbon footprint in the cement industry. The production of clinkers with a dominant representation of belite theoretically makes it possible to reduce carbon emissions by 10 % [6]. The degree of carbonation depends mainly on mineralogy, grain size, water factor, CO₂ concentration and hydration time [7].

2. MATERIAL AND METHODS

2.1. PREPARATION OF RAW MATERIAL MIXTURE

For the preparation of raw material mixture, chemically pure raw materials were used, namely calcium carbonate (CaCO₃, p.a. purity, Penta, Praha, Czech Republic) and silicon dioxide (SiO₂, p.a. purity, Penta, Praha, Czech Republic). The mixture for belite was prepared by mixing 125 g of CaCO₃ with 35 g of SiO₂, which is based on the stoichiometric ratio of calcium and silicon oxides in the C₂S mineral. The raw material mixture was wet ground in a Fritsch Pulverisette 6 planetary mill. Grinding took place in an agate grinding capsule with 25 agate grinding balls with a diameter of 1 cm. The length of grinding was set to 10 minutes and the intensity to 350 rpm. The mixture thus prepared was dried at 105 °C for 12 hours. Drying was carried out in a Binder C 170 laboratory dryer. Compact particles of 2–5 cm size were formed from the mixture during drying.

2.2. FIRING PROCEDURE – GAMMA C₂S

Afterwards, the samples were pour fired in Classic 2017 S superkhantal furnace in two steps. First firing of mixtures was set to 1 250, 1 300, 1 350 and 1 400 °C for 120 minutes. In all cases, the temperature was increased 10 °C min⁻¹ and the cooling proceeded slowly until the furnace cooled down on its own. In this step, calcination of CaCO₃, solid phase reactions and gradual transformation of high-temperature forms of belite to gamma modification occurred. Due to the results achieved, three additional firing procedures were carried out. Specifically, these were firings at 1 450 and 1 500 °C with an isothermal duration of 200 minutes and a firing with a duration of 120 minutes at 1 350 °C and a subsequent duration of 720 minutes at 400 °C during cooling. Then, five grams of each sample were milled in McCrone Micronising Mill for 150 s in 15 ml

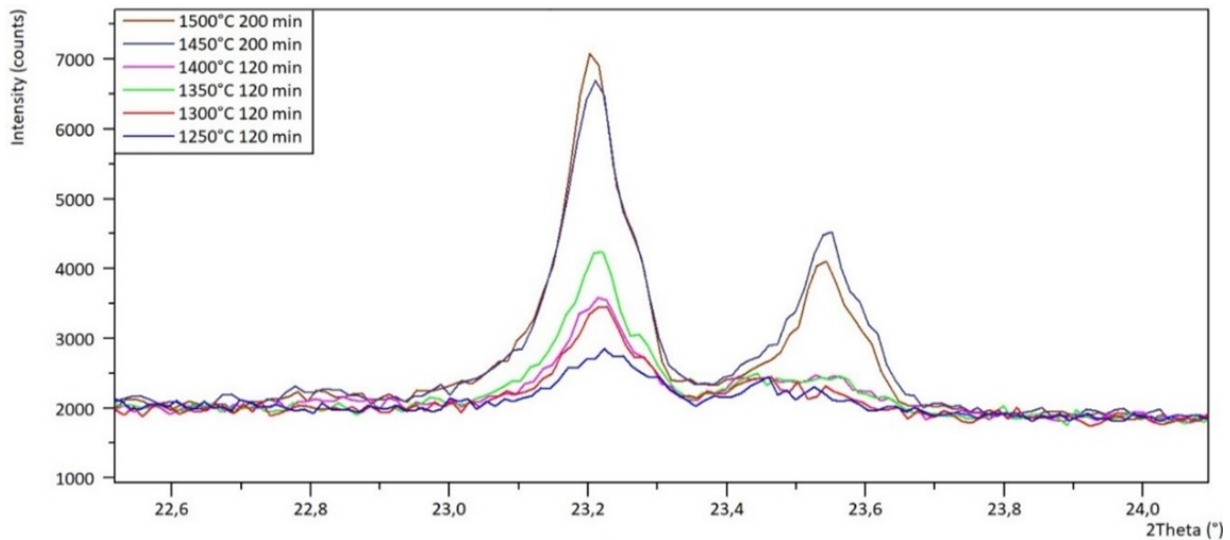


FIGURE 1. Intensities of the diffraction lines of gamma belite at angles $2\theta = 23.2^\circ$ and 23.6° .

of isopropanol to study the effect of particle size in the next step. Each sample was analyzed immediately after firing and milling by XRD and laser granulometry.

2.3. FIRING PROCEDURE – BETA C_2S

Samples prepared by first step firing procedure were immediately fired again. Superkhantal furnace and platinum crucibles were used as well as in the first step. The effect of the second firing was observed on ground and unground samples. In this case, the second firing procedure always took place under the same conditions, namely at 950°C with a duration of 120 minutes and subsequent rapid cooling. During cooling, the samples were gradually taken out of the furnace, poured from the platinum crucibles onto steel sheets and cooled by a stream of compressed air. The only exception is the sample fired at 1250°C , which was not fired a second time because it was not sufficiently reacted. The analysis of the samples after the second firing proceeded in the same way as after the first firing.

2.4. SAMPLE PREPARATION FOR XRD ANALYSIS

After both steps of firing, 5 g of each sample was milled for 150 s with 15 ml of isopropanol in McCrone Micronising Mill to the required fineness for XRD. The PANalytical Empyrean diffractometer (Cu anode, $\lambda = 1.54184 \text{ \AA}$) was used for all XRD analysis. To evaluate the measurements records, the software HighScore plus in combination with ICSD database from 2012 were used. The quantities of mineral phases were determined using the Rietveld method.

2.5. PARTICLE SIZE CHARACTERISATION

Particle size distribution was measured on raw material mixture before firing and then on all samples right after cooling and, in some cases, after addition

milling. Malvern Mastersizer 2000 laser granulometry dry method was used for all analysis.

3. RESULTS AND DISCUSSION

After a series of first firings, the minerals $\beta\text{-}C_2S$, $\gamma\text{-}C_2S$ and also $\text{Ca}(\text{OH})_2$, CaO and SiO_2 were identified in the samples, the presence of which in this case is caused by the low intensity of firing in combination with the selected grain size. The amount of unreacted feedstock ranged from 2 to 16%, with a higher rate of feedstock reaction occurring as the firing temperature increased. Perfect reaction only occurred during additional firings at temperatures of 1450 and 1500°C . It can be confirmed that by firing at higher temperatures and with a longer isothermal hold, a larger amount of $\gamma\text{-}C_2S$ modification is formed upon cooling, which can be observed in Figure 1. This is due to a higher degree of structural ordering and therefore a higher susceptibility to the $\beta \rightarrow \gamma$ polymorphic transformation, which affects the mineralogy and granulometry of the resulting product.

In subsequent second firings, it was confirmed based on XRD analysis that the orthorhombic crystal structure of $\gamma\text{-}C_2S$ can be relatively easily transformed into a monoclinic one, just by using a suitable firing mode. That this structural transformation depends on the size of the particles is illustrated by the comparison of the results of the second firing on ground and unground samples. This is shown in Table 1, which clearly confirms the fact that the smaller $\gamma\text{-}C_2S$ particles convert to $\beta\text{-}C_2S$ more perfectly, as purer $\beta\text{-}C_2S$ samples were always achieved for the milled samples. However, it should be noted that the parameters of the second firing are not sufficient to complete the reaction of the mixture, and the samples still contained the mineral portlandite, CaO and quartz. Their amount corresponded with the amount after the first firing. The statement can be illustrated in

Firing temperature [°C]	After first firing		After second firing			
	β	γ	Unground samples		Ground samples	
	β	γ	β	γ	β	γ
1 300	90.0	10.0	97.5	2.4	98.5	1.5
1 350	81.8	18.2	97.9	2.1	98.2	1.8
1 350 (400)	81.6	18.4	96.1	3.9	99.2	0.8
1 400	82.5	17.5	94.8	5.2	90.1	9.9
1 450	59.0	41.0	81.2	18.8	88.7	11.3
1 500	35.6	64.5	80.5	19.5	88.6	11.4

TABLE 1. Relative representation of beta and gamma belite after firings.

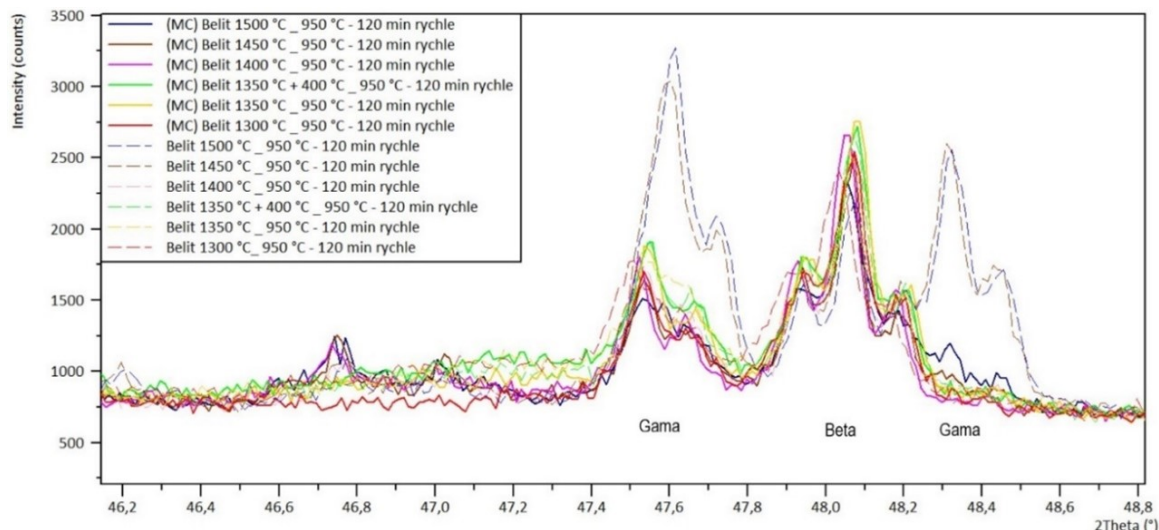


FIGURE 2. Dependence of the structural transformation of belite on the firing regime.

Figure 2, where the intense γ -C₂S lines are still visible in the untreated samples after the second firing.

The average grain size $D(50)$ of the raw material mixture before firing was 12.373 μm . In samples where perfect synthesis did not occur, the particle size decreased to values of 10–11 μm , which can be explained by the calcination of the limestone particles. On the contrary, sufficiently reacted samples, which contain a higher amount of β -C₂S, show a $D(50)$ greater than 16 μm . The average particle size of 13.5 μm was measured in additional firings at temperatures of 1 450 and 1 500 °C. Milled samples had $D(50)$ in the range of values 6.3–8.1 μm . The grains of all samples were slightly reduced due to the second firing procedure. The only exception is the unground sample (1 300 °C), in which the raw materials reacted further, and the grain size increased slightly during the second firing.

4. CONCLUSION

The raw material mixture for belite was prepared at the beginning of the experiment. Then, the γ -C₂S and β -C₂S were produced during two-step firing procedure. Particle size distribution and mineralogical composition were determined for all samples. A belite sample with a total γ -C₂S content of 64.0% was prepared by the described preparation of the raw material mixture and the appropriate amount of supplied energy in

combination with slow cooling. The conducted experiment further confirmed that the mineral belite in the polymorphic beta modification can be created in high purity even without the use of stabilizing ions. The dependence of this transformation on the particle size was also confirmed, but it was proved that the transformation also occurred in the case of grains smaller than 10 μm .

A sample containing a total of 90.0% β -C₂S (ratio β -C₂S: γ -C₂S = 99.2:0.8) was prepared as follows:

- Temperature rise 10 °C min⁻¹, maximum temperature 1 350 °C, duration 120 minutes and slow cooling with duration 720 minutes at 400 °C,
- grinding in a McCrone laboratory mill in the presence of isopropanol,
- temperature rise 10 °C min⁻¹, maximum temperature 950 °C, duration 120 minutes and rapid cooling.

ACKNOWLEDGEMENTS

We acknowledge the financial support to projects, GAČR (Czech Science Foundation) no. 23-05122S and Internal Grand Agency of the Brno University of Technology, Faculty of Civil Engineering no. FAST-S-24-8512.

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