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FORMATION OF BELITE CLUSTERS FROM QUARTZ GRAINS IN PORTLAND CEMENT CLINKER

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ABSTRACT

The conversion process of quartz grains into belite clusters in portland cement clinker has been followed under isothermal heating conditions at 1400°C. On heating, quartz grains are surrounded by layers consisting of belite and liquid, which continue to grow thick with the progress of conversion (outer layers of belite). The conversion process has been divided into three stages considering the chemical composition of the liquid phase formed in each stage. In the first stage are formed two kinds of liquids the compositions of which lie across the primary phase field of wollastonite from each other. The belite crystals precipitated constitute thin, dense layers (inner layers of belite). At the beginning of the second stage, the inside of the belite layers is completely converted into a liquid without quartz and wollastonite. The inner layers extend inward and grow thick; the impurity concentration is lowest for this part of the belite layers. With further progress of diffusion, belite crystals nucleate and grow independently inside the layers. The composition of the coexisting liquid, rich in alkalies, moves on the primary phase field of C_2S toward that of C_3A. In the third stage the conversion is completed and the liquid phase, enriched with Al_2O_3 and Fe_2O_3, is similar in composition to the interstitial liquid in portland cement clinker. The belite crystals, especially those of the inner layers, undergo grain growth with an increase in impurity content with duration of heating. Three kinds of belite crystals different in origin, texture and composition are thus distinguishable in the belite clusters.

Introduction

There have been many studies on the conversion of quartz grains into belite in portland cement clinker as well as in the system CaO - SiO_2 (1-7). Recently, there is an increasing interest in active belite cement for reducing energy consumption in cement making (8-10). Besides, belite cement of low heat evolution has been put to practical use for mass concrete construction. It seems significant, in this view, to reinvestigate the conversion mechanism of quartz grains into belite and the characters of the resulting crystals.

Experimental

The chemical composition of laboratory clinkers to be obtained was as follows: SiO_2 22.94, CaO 66.56, Al_2O_3 5.46, Fe_2O_3 3.04, MgO 0.60, SO_3 0.40, Na_2O 0.40, K_2O 0.60 (wt%). Limestone, clay and chemical reagents were used as starting raw materials; half of the silica component in the clinkers came from reagent silicic anhydride, the mineral composition of which was quartz. The grain size distribution of the silicic anhydride was made so that 85% might be less than 45μm and 15% between 90 and 125μm in diameter. Limestone and clay were passed through a 45μm sieve. The raw mix, pressed into pellets, was heated at 1400°C for given times. Microscopic observations were made in both transmitted and reflected light. Glass specimens of varying CaO/SiO_2 ratios were prepared with *ca.* 9% of Na_2O added; the reflectance (R) was calculated from the refractive index (n) using an equation $R=(n-1)^2/(n+1)^2$. Quantitative spot analyses were made on the liquids and belite crystals with an electron probe microanalyzer (JCMA-733, JEOL, Japan). The chemical formulas of the belite crystals were derived on the assumption Ca+Mg+Na+K = 2. Besides, the elemental distribution maps were prepared for reference.

Results and Discussion

On heating the fine raw mix isothermally at 1400°C, clinkering reaction was completed within a short time around the quartz grains. With active diffusion of CaO toward the quartz grains through the interstitial liquid, layers consisting of belite crystals and liquid resulted with alite as well as free CaO dissolved into the liquid as the source of CaO. These layers was termed "outer layers of belite" to make distinction from "inner layers of belite" to be mentioned later. It was not until the diffusion rate of CaO was lowered to a considerable extent that alite crystals were formed

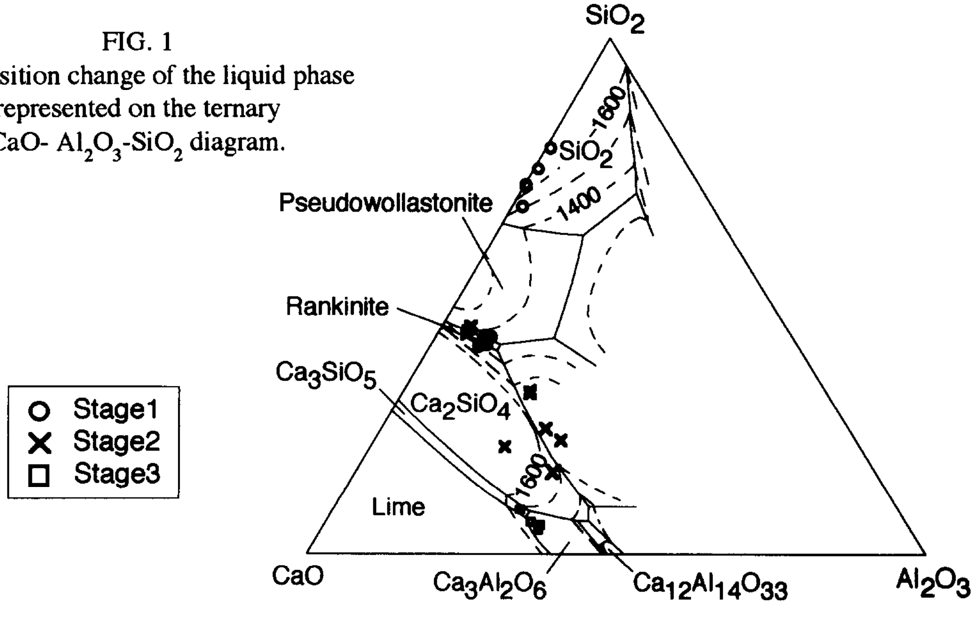


FIG. 1
Composition change of the liquid phase represented on the ternary $CaO-Al_2O_3-SiO_2$ diagram.

TABLE 1
Examples of liquid phase compositions (wt%)

	Stage 1		Stage 2		Stage 3
CaO	12.73	44.03	45.04	28.28	49.95
Fe_2O_3	0.57	2.48	1.00	3.82	12.06
Al_2O_3	0.52	6.03	3.10	16.44	25.49
SiO_2	72.64	40.18	43.63	29.63	5.57
MgO	0.00	1.64	0.83	3.12	2.24
Na_2O	3.50	2.41	2.07	5.53	1.07
K_2O	7.34	1.94	2.98	11.52	2.11
Total	97.30	98.71	98.65	98.34	98.49
C/S	0.18	1.10	1.03	0.95	8.97
C/S*	0.28	1.24	1.14	1.50	9.93

*With Na_2O and K_2O added to CaO

anew on the outer layers. The outer layers grew thick so long as the conversion of the quartz grains was continued and the belite crystals developed to large sizes due to the Ostwald ripening.

With the diffusion of alkalies and CaO, the quartz grains, being converted to cristobalite on their surfaces, were transformed into a liquid phase rich in SiO_2. The liquid increased in CaO/SiO_2 ratio from outside and precipitated lath-shaped psedowollastonite and subsequently belite crystals. With further increase in CaO content, quartz and wollastonite disappeared in this order from inside and eventually belite clusters were completed. The belite crystals were all in the ß phase.

Figure 1 plots the chemical composition of the liquid phase formed at each stage of conversion on the ternary $CaO-Al_2O_3-SiO_2$ diagram. For convenience, MgO, Na_2O and K_2O were reduced and added to CaO, Fe_2O_3 to Al_2O_3 and SO_3 to SiO_2. With the increase in CaO and alkali components in the liquid, the composition moved on the primary phase field of C_2S along the isothermal liquidus curve and finally reached that of C_3A. It seems reasonable, in this view, to divide the conversion process into three stages. In Table 1 are given some representative chemical compositions of the liquid phases in each stage. Figure 2 illustrates the impurity concentration in some of the belite crystals or part of the crystals formed at each stage. The reflectance of the glassy phase in the system $CaO-SiO_2$ changes linearly with the composition, as given in Fig. 3.

Stage 1: Figures 4(a) and (b) exemplifies the conversion textures that appeared within a very short time after heating. A liquid phase of low CaO/SiO_2, wollastonite crystals, another liquid phase of high CaO/SiO_2 and belite crystals occurred in sequence around a quartz grain remaining in the core. On cooling, the liquid phases were transformed into glass. Their compositions are distributed on both sides of the primary phase field of wollastonite (Fig. 1). Both liquids, widely different in reflectance, can easily be distinguished in reflected light, though distinction can hardly be made between the liquid of higher CaO/SiO_2 ratio and wollastonite ($n_X \approx 1.610$, $n_Z \approx 1.651$) because of their close similarity in reflectance (Fig. 3).

Unlike those in the outer layers, the belite crystals, precipitated from the liquid of low supersaturation, were coarse and angular in shape. The crystals were more reactive against etchants than those in the outer layers. Such layers of belite are termed "inner layers of belite." The inner layers initially occurred in contact with the outer layers and were rich in impurity content as

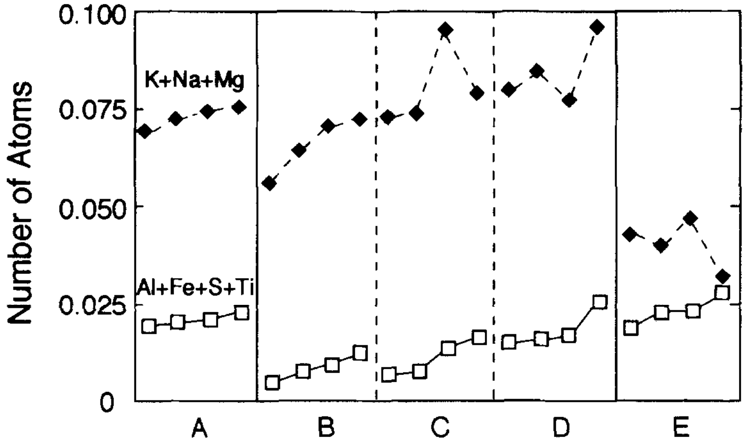


FIG. 2
Impurity concentration in inner layers of belite with the progress of inversion.
A: 1st stage; B,C and D: 2nd stage (D: isolated crystals in the core part);
E: 3rd stage (part formed by Ostwald ripening).

compared with the part grown subsequently (A in Fig. 2). The formation of the inner layers seems to have lowered to a considerable degree the rate of CaO diffusion toward the cores and thus encouraged the occurrence of alite on the outer layers of belite.

An amorphous phase was described to occur transientially in quartz grains in the solid state with incorporation of CaO (2,6). This phase may be compared in composition with the liquid of low CaO/SiO_2 ratio in the present investigation.

Stage 2: This stage begins when the inside of the inner layers is filled entirely with a single liquid phase (Fig. 4(c)). The CaO/SiO_2 ratio of the liquid was higher than 1 (Table 1). With inward growth of the belite layers, depletion of CaO and concentration of the impurity components were clearly recognized on the growth fronts in their X-ray images. Those diffusion boundary layers, about 10μm thick and constitutionally supercooled, caused growth instability as cellular protrusions on the growth fronts of belite crystals. The belite layers formed in this period was highest in purity of all the belite crystals that appeared during the entire process of conversion (B in Fig. 2).

With further increase in CaO concentration, the liquid phase was almost saturated with C_2S toward the core and dendritic belite crystals occurred on quenching (Fig. 4(d)). At the end of this stage belite crystals were nucleated and grown in the core independently of

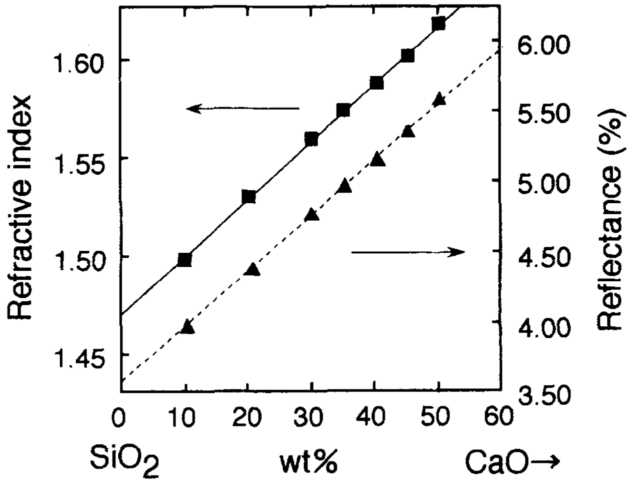
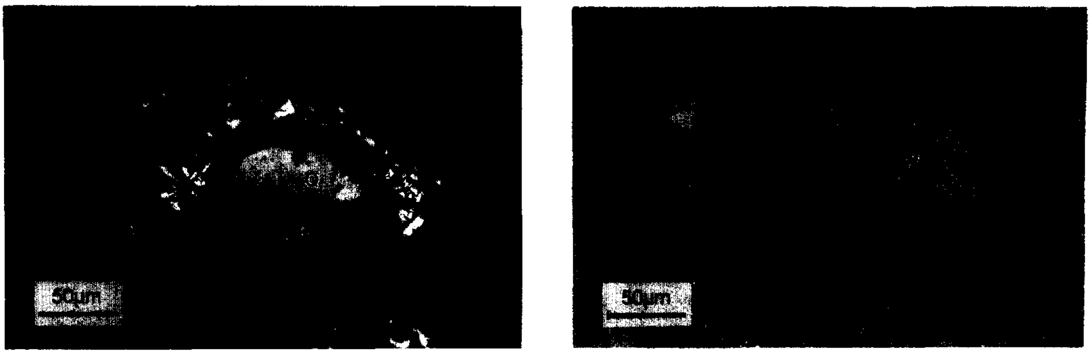
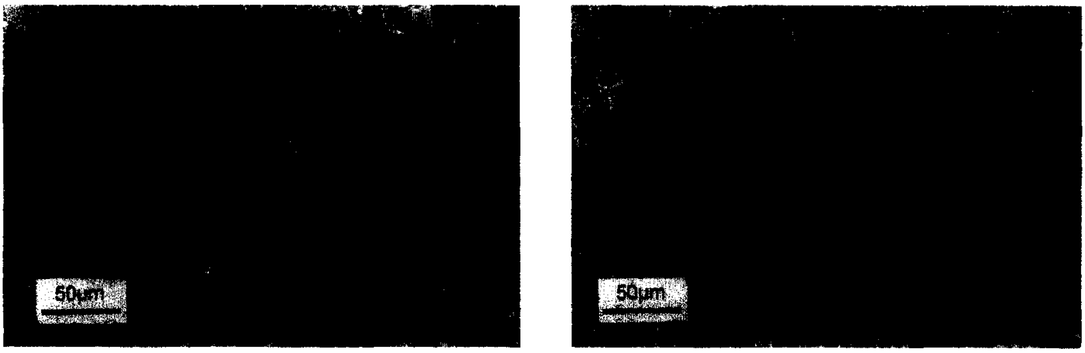


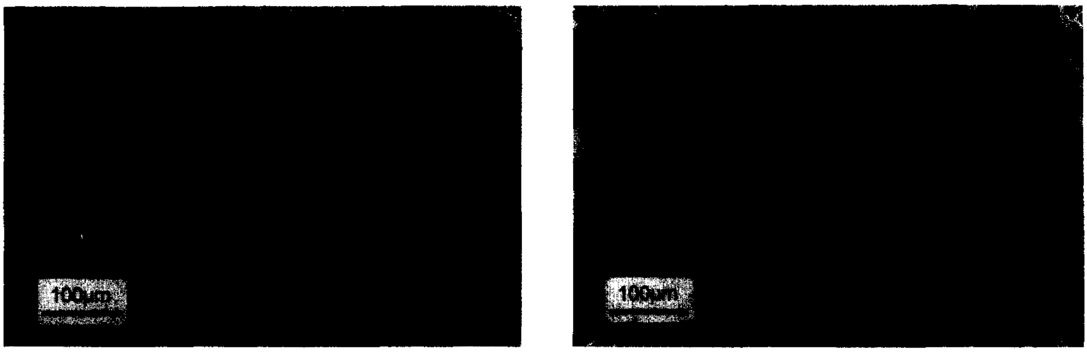
FIG. 3
Refractive index and reflectance of glass in the system $CaO-SiO_2$ (with 9% of Na_2O).



(a) 30 sec (b) 30 sec



(c) 1 min (d) 2 min



(e) 2 min (f) 30 min

FIG. 4
Photomicrographs illustrating the conversion process of quartz grains into belite clusters.
(a) and (b): 1st stage; (c), (d) and (e): 2nd stage; (f): 3rd stage.
Q: quartz, W: wollastonite, I: inner layer of belite, O: outer layer of belite, L: liquid.
(a): crossed polars, (b)-(f): reflected light.

the inner layers (Fig. 4(e)). These crystals, rough grown, gave amoebic appearance without facets. The impurity concentration in belite increases with increasing impurity contents in the liquid (C and D in Fig. 2). The liquid coexisting with belite in this stage was rich in alkalies (Table 1).

Stage 3: In this last stage of conversion, the liquid phase, enriched with Al_2O_3 and Fe_2O_3, was similar in composition to the interstitial liquid in portland cement clinker and, on cooling, differentiated into the crystalline calcium aluminate and calcium aluminoferrite phases (Table 1). The belite crystals underwent Ostwald ripening with an increase in Al_2O_3 and Fe_2O_3 and a decrease in alkalies (E in Fig. 2). This was especially noticeable with belite crystals in the inner layers, which grew at the expense of belite crystals in the outer layers. The change in impurity content can clearly be recognized by the difference in etching behavior within individual crystals (Fig. 4(f)); etching is deeper in the core than in the periphery formed by ripening.

Three kinds of belite different in origin, texture and composition are thus distinguishable from one another in the belite clusters; they are, belite in the outer layers, belite in the inner layers and belite in the cores. It is expected that they differ to some degree in hydraulic behaviors. The conversion of quartz grains occurs involving the neighboring clinker regions and produces belite clusters twice as large as the original quartz grains (3). Accordingly, when quartz grains exist in the raw mix within distances of twice the sum of their radii, they coalesce to form a big belite cluster in clinker. Careful observation, however, makes distinction between individual clusters. The large belite cluster in Fig. 4(f), for example, consists of at least three individuals.

The results in this investigation are applicable to the occurrence of an acidic liquid from finegraind quartz in the raw mix, which reacts with a basic liquid formed in the free lime clusters and leads to the precipitation of alite (2,11,12).

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