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Effect of prolonged heating at elevated temperatures on the phase composition and textures of portland cement clinker

K. Masaki[a,*], I. Maki[b]

[a]*Building Materials Group, Ube Center, Ube-Mitsubishi Cement Research Institute Corporation, 1-6 Okinoyama, Kogushi, Ube 755-8633, Japan*
[b]*Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

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Abstract

Two kinds of portland cement clinker with widely different MgO and SO_3 content were reheated for a long time at elevated temperature. With the clinker rich in MgO and SO_3, alite increased while belite decreased in quantity after reheating. The alite crystals, overgrown with new precipitates, gave zonal structures. Thin platy hexagonal crystals were occasionally nucleated and grown separately in the bulk liquid. High degree of supercooling produced dismembered dendritic crystals of belite. The C/S ratio of the interstitial phase decreased with reheating. The above changes occur in association with the process in which the interstitial liquid, initially variable in basicity, is transformed to the uniform and most acidic one. This process is controlled by the counterdiffusion of CaO and SiO_2, the rate of which is such that, in normal clinker processing, the clinkering reaction terminates before reaching this stage. Rise in firing temperature increases the concentration of SiO_2 in the interstitial liquid and leads to higher solid C_3S/C_2S ratio in clinker. The presence of MgO and SO_3 in abundance lowers the viscosity of the liquid and hence accelerates the changes. No appreciable change could be recognized for the clinker low in MgO and SO_3 content.

Keywords: Alite; Belite; MgO; SO_3; Viscosity

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1. Introduction

With the prolongation of heating at elevated temperatures, portland cement clinkers occasionally undergo noticeable changes in both the phase composition and the morphology of the constituent minerals [1,2]. The most characteristic change is observed for belite crystals, which, initially round in shape, are more or less replaced with dismembered dendrites and decrease in quantity. By contrast, alite increases in quantity, growing on the existing crystals or being nucleated separately to form thin platy crystals in the bulk liquid. Theoretical consideration showed that those changes occur in conjunction with the process in which the interstitial liquid is transformed into the acidic one rich in SiO_2. This process is controlled by the counterdiffusion of CaO and SiO_2 and accelerated by a decrease in viscosity with an increase of MgO and SiO_3 content in the liquid. The results seem significant, in particular, to the production of highly sulfated portland cement clinker coming from the use of fuel rich in sulfur.

2. Materials

Two kinds of portland cement clinker, widely different in MgO and SO_3 content, were used in this study. Table 1 shows their chemical compositions. The clinkers were reheated at 1550 °C for 20 h in air. Clinkers A and B, after reheating, are hereafter denoted as A′ and B′, respectively.

3. Results

Fig. 1(A) and (A′) shows, respectively, the microscopic textures of Clinker A in reflected light before and after reheating. After reheating, the rounded belite grains were almost replaced with fine dendritic belite crystals. The alite crystals were overgrown with new precipitates, which consist of the M_3 phase and appear smooth without

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* Corresponding author. Tel.: +81-836-22-6154; fax: +81-836-22-6189.

E-mail address: 28414u@ube-ind.co.jp (K. Masaki).

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Table 1
Chemical composition of clinkers used in the experiment

Clinker	Insol.	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	F-CaO	Total
A	–	0.28	21.80	5.38	2.74	65.42	2.15	0.94	0.20	0.34	0.32	0.17	0.16	0.50	100.40
B	0.07	0.76	22.13	5.32	3.05	65.76	0.96	0.35	0.22	0.66	0.25	0.16	0.12	0.66	100.47

Insol.: insoluble residue, LOI: loss on ignition.

inclusions. Besides, thin platy alite crystals were occasionally nucleated and grown separately in the bulk interstitial liquid.

Fig. 2 shows the phase composition of Clinkers A and A′ determined by point counting technique. Evidently, alite increased in quantity at the expense of belite. The increment (7.7%) is much higher than 2.0% as expected when 0.5% of free CaO in Clinker A is completely converted to C_3S according to the scheme $C + C_2S = C_3S$.

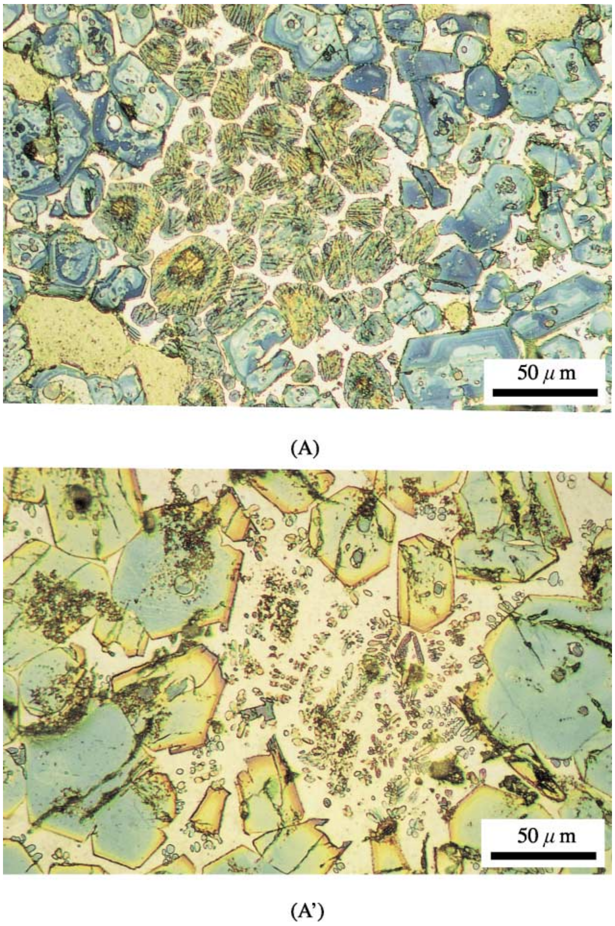
Fig. 3 shows the microscopic textures of Clinker B after reheating (B′). No appreciable texture change could be recognized for both alite and belite before and after reheating.

Table 2 gives the chemical composition of the interstitial phase of Clinker A (as the residue after the treatment with salicylic acid in methanol) before and after reheating. Volatile components as SO_3, Na_2O and K_2O were decreased considerably with the prolongation of heating. The most crucial change consists of the decrease of C/S ratio, which indicates that, with prolongation of heating at elevated temperatures, the interstitial liquid as a whole decreases in basicity and becomes more acidic.

4. Discussion

Fig. 4 shows the cross section of the ternary phase equilibrium diagram of the system $CaO–Al_2O_3–SiO_2$ at 1500 °C, illustrating the formation of portland cement clinker [3,4]. On heating at 1500 °C, there appear in the raw mix innumerable small pockets the phase combinations that vary from D_1 to D_5. The subsequent stage of clinker formation is the formation of C_3S with the reaction between D_1 [CaO clusters: CaO + liquid ($a–b$)] and D_5 [belite clusters: C_2S + liquid ($c–d$)]. With active diffusion of CaO through the liquid phase, the liquid changes its composition toward b along the line $a–b$ in the D_1 region, while in the D_5 region, it is toward c along the line $c–d$; thus, finally resulting with the liquid ($b–c$) saturated with C_3S.

In the initial stage of clinkering, the liquid phases, coexisting in equilibrium with fine CaO and C_2S grains, are supersaturated with CaO and C_2S and their compositions lie, for example, on the dotted lines $a'–b'$ and $c'–d'$. By the same process, there occurs the liquid ($b'–c'$) supersaturated with C_3S, from which precipitate C_3S crystals. With the grain growth of CaO and C_2S, the supersaturation is



(A)

(A')

Fig. 1. Microscopic textures of Clinker A before (A) and after (A′) reheating at 1550 °C for 20 h.

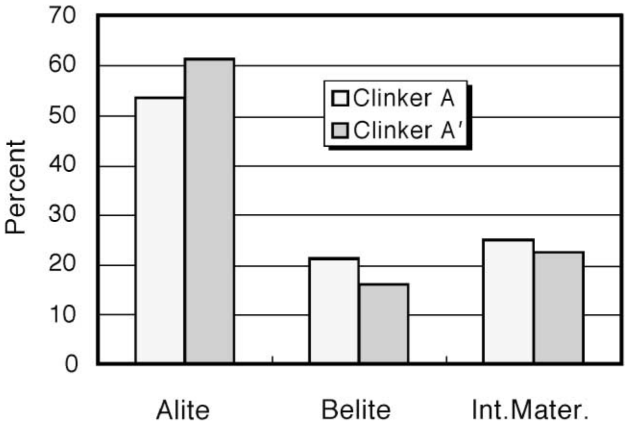


Fig. 2. Phase composition of Clinker A before (A) and after (A′) reheating (determined by point counting technique).

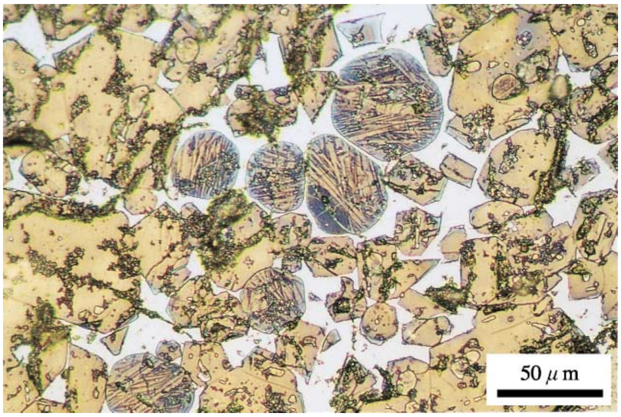


Fig. 3. Microscopic textures of Clinker B after reheating at 1550 °C for 20 h.

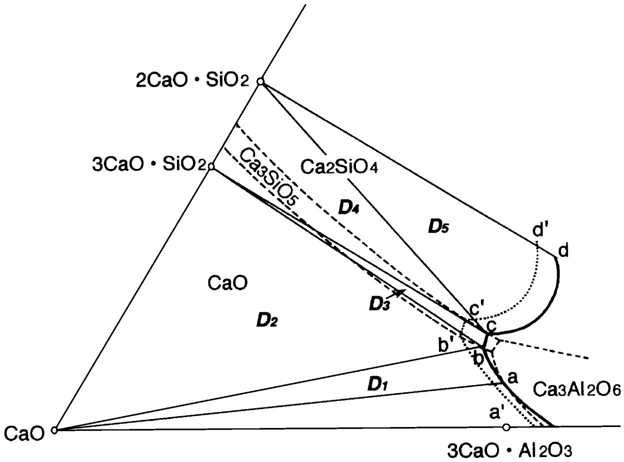


Fig. 4. Cross section at 1500 °C of the ternary $CaO-Al_2O_3-SiO_2$ system relevant to portland cement clinker. Solid lines indicate liquids' curves and broken lines primary phase fields.

lowered and the liquid composition approaches the line *b–c*.

Portland cement clinker, when equilibrium is reached within the compositional triangle D_4, consists of C_3S, C_2S and the liquid with composition *c*. The following changes should therefore be such as to lead to the formation of the uniform interstitial liquid of composition *c* with the reorganization of clinker textures. Those changes are caused by the counterdiffusion of CaO and SiO_2 between the D_2 and D_4 (or D_3) pockets through the liquid phase. With the diffusion of CaO and belite crystals in the D_4 pockets, they are dissolved in the liquid phase and SiO_2 is transported to the D_2 and D_3 pockets to form the liquid of composition *c*. Because of the small CaO and SiO_2 concentration gradient between *b* and *c*, the rate of diffusion is very low and the accompanying changes proceed extremely slowly. The presence of SO_3 and MgO in abundance lowers the liquid viscosity to a considerable degree [5] and hence accelerates the above process. In normal clinker processing, however, the burning time is such that the clinkering reaction is terminated before reaching that stage.

With the rise in heating temperature, the clinker liquid (*c*) assimilates C_2S and increases in quantity (refer to Fig. 4). The CaO/SiO_2 ratio of the liquid decreases with an increase in the solid C_3S/C_2S ratio in the resulting clinker. From the liquid (*c*) saturated with both C_3S and C_2S first precipitate alite crystals on cooling. Usually, the supercooling is not large enough to nucleate new crystallization centers, and the precipitates epitaxially overgrow the existing alite crystals. The crystals grow stably giving zonal structures as well as distinct facets. Large supercooling occasionally causes bulk nucleation in the liquid and produces separate thin platy crystals with cellular defects, the cross section of which appears prismatic under the microscope [6]. With the precipitation of alite, the liquid, enriched with SiO_2, becomes higher in viscosity and tends to supercool considerably. The silica component produces blocked volumes in the interstitial liquid, the concentration of which rises with decreasing temperature and hence causes anomalous viscosity increase [7]. Dendritic belite crystals thus precipitate under high degree of supercooling. Such mode of belite precipitation is in great contrast with the Ostwald ripening, leading to the formation of large rounded belite grains during the initial stage of clinkering. The mechanism of crystallization and the morphology of those alite and belite crystals are very much like those in fused portland cement clinker [8]. Fig. 5 shows how the liquid saturated with C_2S supercools. In this figure, dendritic belite crystals grow on the surface of alite crystals, with belite grains formed by decomposition as nuclei. Considering that the decomposition of alite occurs below 1250 °C, the liquid can supercool at least down to this temperature.

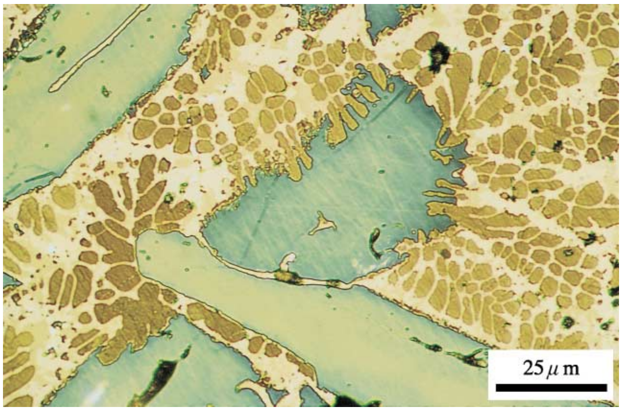


Fig. 5. Dendritic belite crystals grown on the decomposed surface of alite crystals in fused portland cement clinker.

Table 2
Chemical composition of the interstitial phase before (A) and after (A′) reheating[a]

Clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	MnO	Total	C/S
A	7.24	21.57	12.18	47.39	5.48	3.81	0.43	1.42	0.46	100.00	6.55
A′	9.69	22.83	12.41	49.27	5.37	0.17	0.14	0.05	0.47	100.00	5.08

[a] Insol. and LOI were excluded from the sum.

Acknowledgments

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