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THERMOELASTICITY OF BELITE IN PORTLAND CEMENT CLINKER

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ABSTRACT

Belite crystals, separated from an industrial cement clinker, were examined by high-temperature powder X-ray diffractometry. We determined the starting and finishing temperatures of the α'_L-to-β martensitic transformation and those of the reverse (β-to-α'_L) transformation. The thermal hysteresis was negative (−65°C), indicating the thermoelasticity of the transformation. Each of the transformation temperatures was lower than that of pure Ca_2SiO_4. Because the finishing temperature of the α'_L-to-β transformation was higher than ambient temperature, the α'_L-phase was entirely inverted to the β-phase during cooling. © *1998 Elsevier Science Ltd*

Introduction

The α'_L-to-β transformation of Ca_2SiO_4 (C_2S) and C_2S solid solutions (C_2Sss) has been considered to be martensitic (1–5). Recently, the transformation has been reported to be thermoelastic (6,7). One of the main characteristics is the negative thermal hysteresis (A_s–M_s), where A_s and M_s are the starting temperatures of the reverse (β-to-α'_L) and forward transformations, respectively. Because of the athermal nature of the transformation, the amount of transformation remains unchanged when the temperature is kept constant. Thus these transformation temperatures have been successfully determined by high-temperature X-ray diffractometry (HT-XRD) for C_2Sss doped with SrO (6) and by high-temperature optical microscopy for C_2Sss doped with Na_2O, Al_2O_3, and Fe_2O_3 (7). The α'_L and β-phases coexisted within the temperature intervals between M_s and M_f during cooling and between A_s and A_f during heating, where M_f and A_f are the finishing temperatures of the forward and reverse transformations, respectively.

When a belite crystal with impurities is cooled from the stable temperature region of the α-phase, it decomposes into a liquid and the α'_H-phase crystal that is lower in impurity concentration than the parent α-phase (8–12). This process is called the remelting reaction of belite. The reaction is always preceded by the α-to-α'_H polymorphic transition, which forms six sets of the α'_H-phase lamellae without a change in chemical composition (13,14). The microtextures caused by the remelting reaction are mostly dependent on the Al/Fe ratio of the parent α-phase as well as on the temperature (10,15). The parent crystals with Al/Fe >

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1 produced liquids, which readily spread on the lamellae, leading to the high rate of disintegration of the intracrystalline lamella structure. After the reaction, successive transitions of $\alpha'_H \rightarrow \alpha'_L \rightarrow \beta$ occurred upon further cooling.

In normally processed cement clinkers, most of the belite crystals are composed of the β-phase, indicating that the α'_L-to-β transformation usually occurs during cooling. In spite of the importance of the martensitic transformation, the thermoelasicity of the belite crystals in industrial cement clinkers has not yet been clarified. In the present study, we determined the transformation temperatures by HT-XRD and indicated the thermoelasticity as evidenced by the negative thermal hysteresis.

Experimental

Microscopic observations were made in both transmitted and reflected light for industrial cement clinkers. Rapidly quenched belite crystals, in which the remelting reaction did not occur, could be readily recognized from the intracrystalline microtextures at the optical microscopic level (15). We selected such industrial cement clinkers that included the rapidly quenched belite crystals.

These belite crystals were separated by dissolving the alite crystals with a methanol solution of trimethylacetic acid at 25°C (16), and dissolving the interstitial materials with an aqueous solution of KOH and saccharose at 95°C (17). Each treatment was repeated three times with intermediate grinding. The compositions of the extract were determined by chemical analysis.

The phase constitution was examined using an X-ray powder diffractometer (Model PW3050, Philips Co.) equipped with a heating stage (Model HTK, Anton Paar Co.). The profile data were collected using monochromatized Cu*K*α radiation (50 kV, 40 mA) and a step-scan technique (step width = 0.02° and fixed time = 1 s) in the 2θ range from 30° to 35°. The powder specimens were mixed with Au powder as an internal temperature standard (18). They were deposited with ethyl alcohol on the platinum heating filament (132 mm × 9 mm × 1 mm). A programmable divergence slit was employed to maintain an illumination area of 5 mm × 9 mm on the sample regardless of the 2θ value. From the change in the phase constitution during the stepwise heating to 600°C (step width = 10°C), we determined A_s and A_f. At each step, the sample temperature was maintained for 15 min. during data collection. After the heating experiment, the sample, in which the remelting reaction occurred during heating above A_f, was changed to the next one. This sample was rapidly heated to 550°C (above A_f) and rapidly cooled to 400°C (stable temperature region of the α'_L-phase), followed by a similar stepwise cooling to 25°C for the determination of M_s and M_f.

Results and Discussion

Chemical Composition and Microtexture

From the oxide components determined by the wet chemical analysis (Table 1), the chemical formula has been derived assuming Ca + Mg + Na + K = 2 as follows: $(Ca_{1.95}Mg_{0.02}Na_{0.01}K_{0.02})_{\Sigma 2}(Si_{0.95}Al_{0.05}Fe_{0.02}S_{0.01})_{\Sigma 1.03}O_{4.01}$ (Al/Fe = 3.3 > 1). Because the Al/Fe ratio is larger than unity, the remelting reaction must readily occur when heated in the stable temperature region of the α'_L-phase. However, from microscopy, the crystals used for

TABLE 1
Chemical composition of belite extract (wt%).

Substance	Composition
LOI	1.20
Insol.	0.14
SiO_2	32.57
Al_2O_3	1.48
Fe_2O_3	0.70
CaO	62.12
MgO	0.45
SO_3	0.33
Na_2O	0.21
K_2O	0.56
MnO	0.06
Total	99.82

the HT-XRD cooling experiment showed no evidence for occurrence of the remelting reaction due to the very short heating time above M_s. Thus, a convincing result is expected for M_s and M_f.

Phase Constitution at High Temperatures and Transformation Temperatures

The belite extract was entirely composed of the β-phase. During stepwise heating from 325°C, the α'_L-phase first appeared at 335°C. Accordingly, we determined As to be 330 ± 5°C. The relative amount of the α'_L-phase steadily increased during further heating. A very small amount of the β-phase was detected at 540°C, while the sample was completely inverted to the α'_L-phase at 550°C. Accordingly, we determined A_f to be 545 ± 5°C. Figure 1 shows the series of XRD patterns during heating from 325°C to 550°C.

The M_s and M_f values were determined in a similar manner and are summarized in Table 2, together with A_s and A_f. These temperatures were lower than the corresponding values of pure C_2S, in accordance with the previous results (6,7). Because M_f was higher than ambient temperature, the belite crystals were entirely inverted to the β-phase during cooling.

Thermal Hysteresis and Temperature Intervals of M_s–M_f and A_f–A_s

The thermal hysteresis was negative (Table 2), indicating the thermoelasticity of the transformation. This value (−65°C) is comparable to that of SrO-doped C_2Sss with Sr/(Sr+Ca) = 0.07 (6), in which the hysteresis steadily decreased from 80°C to −75°C with increasing Sr/(Sr+Ca) ratio from 0.02 to 0.08. For C_2Sss doped with Na_2O, Al_2O_3, and Fe_2O_3 (7), the hysteresis also steadily decreased from −20°C to −50°C with the increment of the concentration of foreign oxides.

With pure C_2S, the M_s and A_s could be determined by differential thermal analysis (DTA) (19). The small temperature intervals of both M_s–M_f and A_f–A_s (Table 2) made possible the detection of these transformation starting temperatures. In previous studies (6,7), both intervals showed a tendency to increase with increasing concentration of foreign oxides.

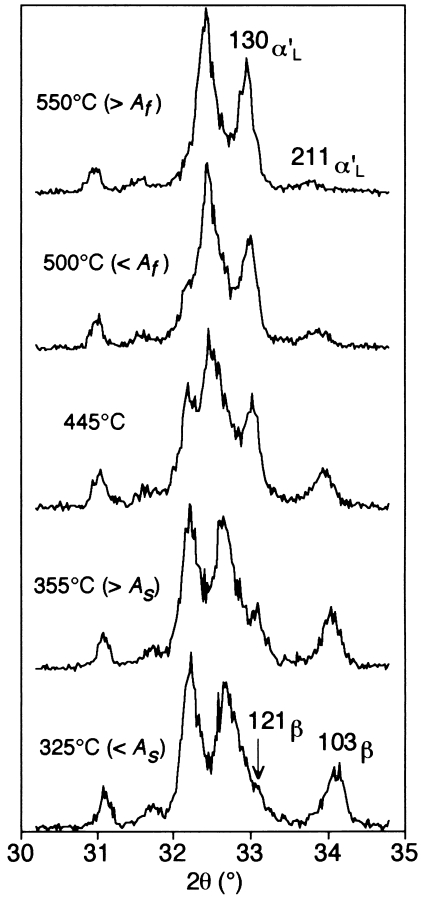

FIG. 1.
High-temperature XRD patterns during heating. The nucleation of the α'_L-phase within the host β-phase was detected from the $130_{\alpha'L}$ reflection. The completeness of the β-to-α'_L transformation was detected by the disappearance of the 103_β reflection.

TABLE 2
Transformation temperature of belite and pure Ca_2SiO_4.

	Temperature (°C)*				Hysteresis	Temperature Interval	
Sample	A_s	A_f	M_s	M_f	A_s–M_s	M_s–M_f	A_f–A_s
Belite	330	545	395	160	−65	215	235
Ca_2SiO_4	710	740	680	610	30	70	30

*Estimated errors are ±5°C.
#Transformation temperatures given by Fukuda et al. (6).

When the intervals are relatively large as in the present belite crystal, these temperatures are no longer detectable by conventional DTA. Under these circumstances, the HT-XRD would be one of the most effective methods for the determination of both starting and finishing temperatures.

Conclusions

The thermal hysteresis (A_s–M_s) was negative, indicating the thermoelasticity of the α'_L-to-β martensitic transformation.

All of the starting and finishing temperatures of the $\alpha'_L \leftrightarrow \beta$ transformations (M_s, M_f, A_s, and A_f) were lower than the corresponding values of pure Ca_2SiO_4.

Both temperature intervals of M_s–M_f and A_f–A_s were much larger than those of pure Ca_2SiO_4.

Because M_f was higher than ambient temperature, the α'_L-to-β transformation was completed during cooling.

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References

1. G.W. Groves, J. Mat. Sci. 16, 1063 (1981).
2. G.W. Groves, Cem. Concr. Res. 12, 619 (1982).
3. G.W. Groves, J. Mat. Sci. 18, 1615 (1983).
4. P. Barnes and A. Ghose, Structure and Performance of Cements, P. Barnes (ed.), pp. 139–203, Applied Science Publishers, U.K., 1983.
5. Y.J. Kim, I. Nettleship, and W.M. Kriven, J. Am. Ceram. Soc. 75, 2407 (1992).
6. K. Fukuda, I. Maki, and S. Ito, J. Am. Ceram. Soc. 79, 2969 (1996).
7. K. Fukuda, I. Maki, and S. Ito, J. Am. Ceram. Soc. 79, 2925 (1996).
8. K. Fukuda, I. Maki, and S. Ito, J. Am. Ceram. Soc. 75, 2896 (1992).
9. K. Fukuda, I. Maki, S. Ikeda, and S. Ito, J. Am. Ceram. Soc. 76, 2942 (1993).
10. K. Fukuda, I. Maki, S. Ito, H. Yoshida, and C. Kato, J. Am. Ceram. Soc. 77, 3027 (1994).
11. K. Fukuda, I. Maki, S. Ito, and H. Yoshida, J. Am. Ceram. Soc. 78, 3387 (1995).
12. K. Fukuda, I. Maki, S. Ito, and K. Toyoda, J. Ceram. Soc. Jpn. 103, 444 (1995).
13. K. Fukuda and I. Maki, Cem. Concr. Res. 19, 913 (1989).
14. K. Fukuda and I. Maki, Cem. Concr. Res. 23, 599 (1993).
15. K. Fukuda, I. Maki, and S. Ito, Proc. 10th Int. Congr. Chem. Cem. 1, 1i052, 1997.
16. K. Hiraiwa, S. Ito, and I. Maki, Proc. 51st Annual Meet. Cem. Assoc. Jpn. 2–3 (1997).
17. W.A. Gutterridge, Cem. Concr. Res. 9, 319 (1979).
18. R.O. Simmons, J. Appl. Phys. 41, 2235 (1970).
19. G. Yamaguchi, Y. Ono, S. Kawamura, and Y. Soda, J. Ceram. Assoc. Jpn. 71, 105 (1963).