Pergamon

Cement and Concrete Research 31 (2001) 1185–1189

CEMENT AND CONCRETE RESEARCH

Remelting reaction of α-Ca_2SiO_4 solid solution confirmed in Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ pseudobinary system

Koichiro Fukuda[a],*, Ayari Takeda[a], Hideto Yoshida[b]

[a]*Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*
[b]*Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan*

Received 18 August 2000; accepted 30 April 2001

Abstract

A phase equilibrium diagram was determined for the P_2O_5-bearing Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ pseudobinary system. The diagram provided evidence for the occurrence of the remelting reaction in the α-Ca_2SiO_4 solid solution (C_2S(ss)) during cooling. The reaction started at 1395°C immediately after the α-to-α_H' transition and finished at 1348°C. The decomposition products at 1395°C were made up of $\sim$2.4 mass% of liquid and $\sim$97.6 mass% of solid α'-C_2S(ss). The exsolved liquid was composed of $\sim$20.8 mass% of Ca_2SiO_4 and $\sim$79.2 mass% of $Ca_{12}Al_{14}O_{33}$, corresponding to Al_2O_3 $\sim$40.7 mass%, CaO $\sim$52.0 mass%, and SiO_2 $\sim$7.3 mass%. From the liquid coexisting with α-C_2S(ss) above 1395°C, the α'-phase crystals were newly precipitated in association with the remelting reaction. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ca_2SiO_4; Characterization; Petrography; Reaction; Remelting

1. Introduction

The remelting reaction is an unusual decomposition reaction, in which a solid decomposes into another solid and a liquid during cooling. With the silicates other than the Ca_2SiO_4 solid solutions (C_2S(ss)), the reaction has never been reported. When α-C_2S(ss) with a large amount of impurities is cooled from its stable temperature region, it decomposes into a liquid and the α'_H-C_2S(ss), which has a lower impurity concentration [1–6]. The reaction is always preceded by the α-to-α'_H polymorphic transition, which forms six sets of α'_H-phase lamellae without a change in chemical composition [7–9]. The subsequent remelting reaction requires an atomic diffusion process, thus it can be depressed by rapid quenching.

The reaction has been applied to improve the hydration activity and grindability of the belite-rich cement [10–12]. The modified cement was mainly composed of the belite in which the remelting reaction had sufficiently occurred, and thus distinct from the conventional belite-rich cement. In normal Portland cement clinkers, the belite crystals sometimes show microtextures induced by remelting, especially when the clinkers were slowly cooled [6]. These microtextures carry a wealth of information on the processing conditions during cooling. Thus, the thermal history of the clinkers would be deducible from the quantitative information about the reaction products.

The present study deals with the preparation of the pseudobinary phase diagram for the Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ system, which gives thermodynamic evidence for the remelting reaction of C_2S(ss). This diagram also provides quantitative information on the chemical compositions of the reaction products, their relative amounts, and transformation temperatures.

2. Experimental

2.1. Materials

Two types of starting materials, $(Ca_{1.985}\square_{0.015})(Si_{0.970}P_{0.030})O_4$ and $Ca_{12}Al_{14}O_{33}$, were synthesized by solid-state reactions. Appropriate amounts of reagent-grade

---

* Corresponding author. Tel.: +81-52-735-5289; fax: +81-52-735-5294.

E-mail address: fukuda@mse.nitech.ac.jp (K. Fukuda).

PII: S0008-8846(01)00537-3

Table 1
Heating temperature and phase constitution[a]

Sample	$C_2S(ss)^b/Ca_{12}Al_{14}O_{33}$ (mass ratio)	Temperature (°C)	Duration (h)	Phases
S-1	1.50	1700	2	α + liquid
S-2	1.50	1600	25	α + liquid
S-3	1.50	1500	20	α + liquid
S-4	1.00	1400	100	α + liquid
S-5	1.00	1390	22	α' + liquid
S-6	0.43	1375	165	α' + liquid
S-7	0.43	1350	94	α' + liquid
S-8	0.43	1349	60	α' + liquid
S-9	0.43	1347	1	$\alpha' + Ca_{12}Al_{14}O_{33}$
S-10	0.43	1300	72	$\alpha' + Ca_{12}Al_{14}O_{33}$

[a] Both α'_H and α'_L are represented by α'.
[b] $(Ca_{1,985}\square_{0.015})(Si_{0.970}P_{0.030})O_4$.

chemicals, $CaCO_3$, SiO_2, Al_2O_3, and $CaHPO_4 \cdot 2H_2O$, were ground in an agate container of a planetary micromill (Model P6, Fritsch, Idar-Oberstein, Germany), calcined at 1200°C for 1 h, and then quenched in air. A small amount of P_2O_5 was added to prevent disintegration of the $C_2S(ss)$ crystals due to the β-to-γ phase transition during quenching. These two materials were mixed in various ratios as given in Table 1, isothermally heated at temperatures between 1700°C and 1300°C for more than 1 h, and then rapidly quenched in cold water. The obtained samples were termed S-1 to S-10 in the order of decreasing preparation temperature.

2.2. Characterization

Polished sections were prepared for all the samples and their microtextures were observed using an optical microscope. The phase constitution was examined by powder X-ray diffractometry (XRD, model PW3050, Philips Analytical X-ray, Almelo, The Netherlands). The $C_2S(ss)$–liquid compositional pairs above 1350°C (samples S-1 to S-7 in Table 1) were analyzed in order to obtain data for the phase diagram preparation. Quantitative spot analyses were made using an electron probe microanalyzer (EPMA, model JCMA-733, JEOL, Tokyo, Japan) on both $C_2S(ss)$ and liquid (a glass at ambient temperature) 20 μm from the crystal–liquid interface (accelerating voltage, 15 kV; specimen current, 0.012 μA; electron probe diameter, 1 μm). The correction was made by the ZAF routines.

3. Results and discussion

3.1. Phase constitution

The $C_2S(ss)$ crystals heated at 1400°C or above (samples S-1 to S-4) showed the intracrystalline lamella structure induced by the α-to-α'_H transition [7–9]. This implies that these crystals were originally formed in the stable temperature region of the α phase. On the other hand, the crystals heated at 1390°C or below (S-5 to S-10) showed a polysynthetic twinning formed by the α'_L-to-β transition during quenching [13,14], indicating that the phase compositions at these temperatures were α'_H or α'_L. At 1349°C or above, the interstitial material was in a liquid state (S-1 to S-8). XRD showed that the $Ca_{12}Al_{14}O_{33}$ and $C_2S(ss)$ crystals coexisted at 1347°C or below (S-9 and S-10). As a result, the phase constitution at elevated temperatures is summarized in Table 1, in which no phase distinction is made between α'_H and α'_L, and both phases are simply represented by α'.

From Table 1, we determined the transformation temperature between α and α' to be ~1395°C, which is lower than that of pure Ca_2SiO_4 (1425°C [15]). However, it is higher than the corresponding transformation temperatures of $C_2S(ss)$ doped with Fe_2O_3 in previous studies (1290°C

Table 2
Numbers of atoms in $C_2S(ss)$[a]

Sample	S-1	S-2	S-3	S-4	S-5	S-6	S-7
Ca	1.964(6)	1.960(11)	1.966(7)	1.968(8)	1.96(1)	1.96(1)	1.96(1)
Al	0.015(3)	0.018(6)	0.014(4)	0.011(4)	0.02(1)	0.013(10)	0.013(8)
$\sum$	1.979(4)	1.978(5)	1.980(3)	1.980(5)	1.97(1)	1.97(2)	1.97(2)
Si	0.940(12)	0.942(14)	0.933(10)	0.911(13)	0.96(2)	0.96(1)	0.96(1)
P	0.044(9)	0.042(7)	0.046(5)	0.059(9)	0.04(3)	0.04(6)	0.039(5)
Al	0.017(5)	0.016(8)	0.021(6)	0.030(4)	–	–	–
$\sum$	1	1	1	1	1.00(1)	1.00(1)	1.00(1)
0	4	4	4	4	4	4	4

[a] Figures in parentheses indicate standard deviations.

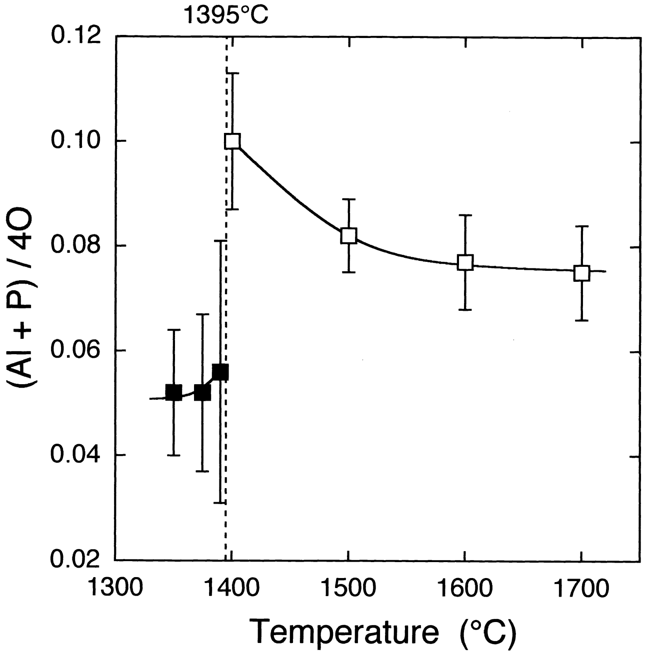

Fig. 1. Total number of Al and P atoms determined on the basis of four oxygen atoms as a function of temperature. The α-to-α′ phase transition occurs at ~ 1395°C. (□) α- and (■) α′-C_2S(ss).

[5] and 1280°C [16]). The interstitial liquid, which is rich in the $Ca_{12}Al_{14}O_{33}$ component, is presumably formed at ~ 1348°C. This is ~ 70°C lower than the melting point of $Ca_{12}Al_{14}O_{33}$ (1415°C).

3.2. Chemical compositions of C_2S(ss) and coexisting liquid

From the oxide compositions of C_2S(ss) determined by EPMA, the chemical formulas have been derived on the basis of four oxygen atoms in one formula unit (Table 2). For the α′-phase crystals (S-5 to S-7), the sum total of the Si and P atoms becomes nearly unity. Thus, all Al atoms would go to the Ca sites, and ~ 1.5% of the Ca sites are left vacant. On the other hand, Al atoms in the α-phase crystals (S-1 to S-4) probably occupy both the Ca and Si sites. Based on the assumption that the Si sites are entirely fulfilled by Si, P, and Al atoms, the residual Al atoms occupy the Ca sites while ~ 1.0% of the Ca sites remain vacant.

With decreasing temperature from 1700°C to 1400°C, the sum total of the Al and P atoms in the α-phase steadily increased from 0.075 to 0.1 (Fig. 1). The sum total of these atoms in the α′-phase crystals remained almost constant (~ 0.05) irrespective of temperature, being lower than those in the α phase.

Table 3
Chemical composition of liquids[a]

Sample	S-1	S-2	S-3	S-4	S-5	S-6	S-7
SiO_2	17.7(3)	13.0(5)	9.6(4)	7.8(1)	7.42(8)	6.9(1)	6.23(7)
CaO	55.6(3)	52.7(3)	50.8(2)	50.6(1)	50.9(1)	50.9(1)	50.6(1)
Al_2O_3	25.4(5)	33.2(9)	38.4(5)	40.4(3)	40.5(1)	41.3(2)	42.0(1)
P_2O_5	1.4(1)	1.2(2)	1.1(2)	1.2(2)	1.2(1)	0.9(2)	1.2(1)

[a] Total is normalized to be 100 mass%.

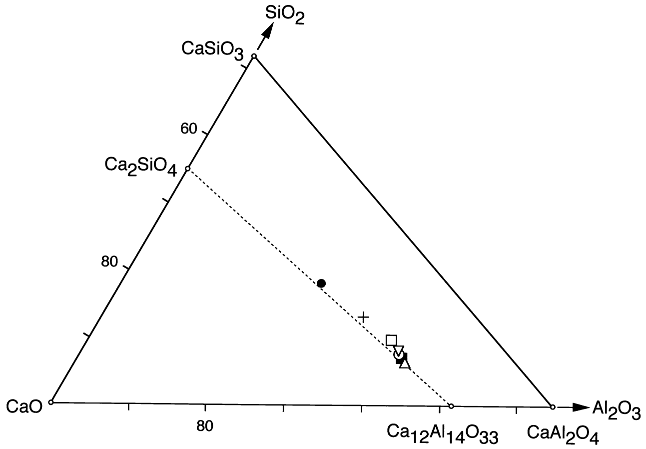

Fig. 2. Compositions of liquids coexisting with C_2S(ss) crystals on a portion of the $CaO-SiO_2-Al_2O_3$ ternary system. (●) 1700°C, (+) 1600°C, (□) 1500°C, (▽) 1400°C, (○) 1390°C, (■) 1375°C, and (△) 1350°C. The liquids have compositions almost along $Ca_2SiO_4-Ca_{12}Al_{14}O_{33}$.

The chemical compositions of the liquids coexisting with C_2S(ss) are summarized in Table 3. The concentration of P_2O_5 was so low that the liquid compositions were represented on the $CaO-SiO_2-Al_2O_3$ ternary diagram (Fig. 2). In this figure, all the liquid compositions lie nearly on the tie line between Ca_2SiO_4 and $Ca_{12}Al_{14}O_{33}$; the $Ca_{12}Al_{14}O_{33}$ content steadily increased from ~ 50 to ~ 83 mass% as the temperature decreased from 1700°C to 1350°C. This is in accord with the liquidus field of Ca_2SiO_4 extending toward

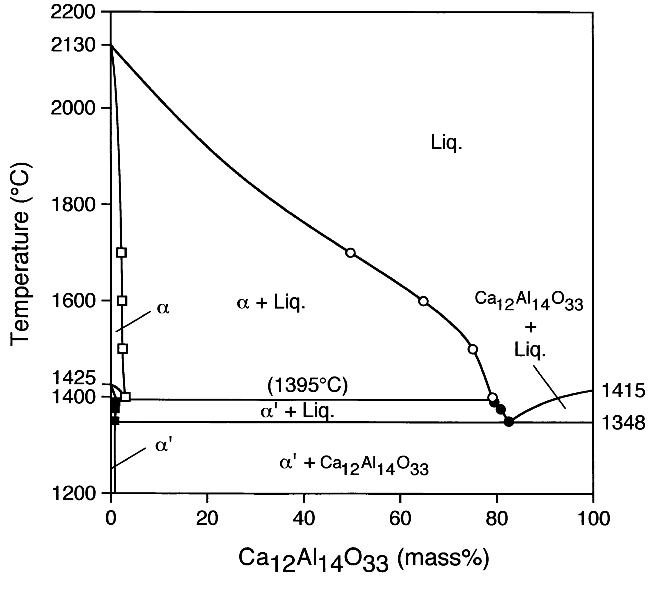

Fig. 3. Phase relationships in the $Ca_2SiO_4-Ca_{12}Al_{14}O_{33}$ pseudobinary system. (□) α- and (■) α′-C_2S(ss). (○ and ●) liquid phases.

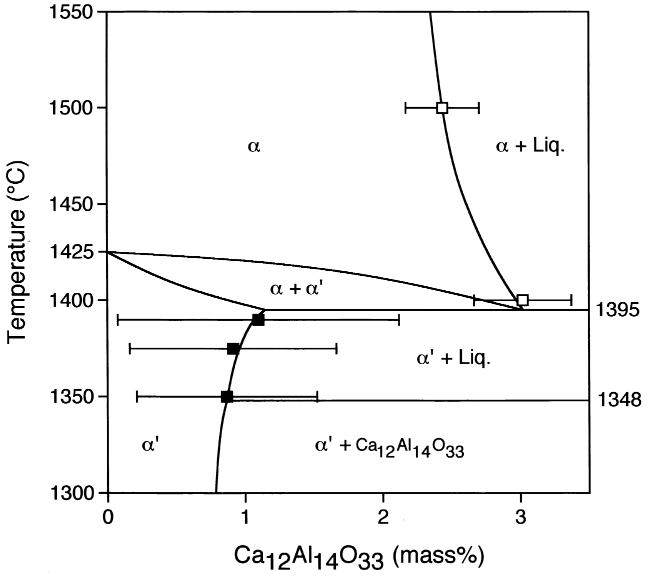

Fig. 4. Part of the Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ system in Fig. 3, illustrating that the single α-phase can decompose into the two-phase mixture of α′ and liquid upon cooling.

$Ca_{12}Al_{14}O_{33}$ in the ternary phase diagram determined in a previous study [17].

3.3. Phase diagram of P_2O_5-bearing pseudobinary system Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$

Because the liquids coexisting with C_2S(ss) changed its chemical composition along the tie line Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ (Fig. 2), we established the phase diagram of this pseudobinary system (Fig. 3). Fig. 4 shows a blow-up of the portion in Fig. 3, indicating that the α-phase crystals, when cooled to 1395°C, start to decompose into a liquid (2.4 mass%) and the α′-phase crystals (97.6 mass%), which are lower in $Ca_{12}Al_{14}O_{33}$ concentration. The liquid is composed of ~20.8 mass% of Ca_2SiO_4 and ~79.2 mass% of $Ca_{12}Al_{14}O_{33}$ (Al_2O_3 ~40.7 mass%, CaO ~52.0 mass%, and SiO_2 ~7.3 mass%). With decreasing temperature, the $Ca_{12}Al_{14}O_{33}$ content in the exsolved liquid steadily increases, and finally reaches its maximum value of ~82.5 mass% (Al_2O_3 ~42.5 mass%, CaO ~51.4 mass%, and SiO_2 ~6.1 mass%) at the eutectic temperature of 1348°C, below which the remelting reaction ceases.

The phase diagram (Fig. 3) shows another reaction that is accompanied by remelting [6]. When the liquid coexisting with α-C_2S(ss) is cooled below 1395°C, it precipitates the α′-phase crystals, the $Ca_{12}Al_{14}O_{33}$ component of which is ~1 mass%. In our previous study [2], such α′-phase crystals were observed by optical microscopy to overgrow the remelting C_2S(ss) crystals.

The phase equilibrium diagram in Fig. 3 shows a direct transformation of the $\alpha \rightarrow \alpha' +$liquid, which is also confirmed in our previous study in the Ca_2SiO_4–$CaFe_4O_7$ pseudobinary system [5]. This transformation, however, seems to require a large activation energy. Accordingly, the polymorphic α-to-α′ phase transition first occurs upon cooling, leading to the formation of the lamella structure within the crystals. After the transition, the liquid heterogeneously exsolves on the lamella boundaries due to the favorable activation energy for nucleation [1].

4. Conclusions

1. We established the pseudobinary phase diagram of the Ca_2SiO_4–$Ca_{12}Al_{14}O_{33}$ system to show the occurrence of the remelting reaction in α-C_2S(ss).
2. The reaction started at 1395°C and finished at 1348°C during the cooling process.
3. The liquid exsolved by the remelting reaction was rich in the $Ca_{12}Al_{14}O_{33}$ component. At 1395°C, it was composed of ~20.8 mass% of Ca_2SiO_4 and ~79.2 mass% of $Ca_{12}Al_{14}O_{33}$ (Al_2O_3 ~40.7 mass%, CaO ~52.0 mass%, and SiO_2 ~7.3 mass%).
4. With decreasing temperature, the $Ca_{12}Al_{14}O_{33}$ content in the exsolved liquid steadily increased. The final composition at 1348°C was ~17.5 mass% of Ca_2SiO_4 and ~82.5 mass% of $Ca_{12}Al_{14}O_{33}$ (Al_2O_3 ~42.5 mass%, CaO ~51.4 mass%, and SiO_2 ~6.1 mass%).
5. With decreasing temperature, the concentration of foreign oxides (Al_2O_3 and P_2O_5) in the α-C_2S(ss) increased, while it remained almost constant in α′-C_2S(ss).

Acknowledgments

K.F. is grateful to Japan Cement Association for financial support.

References

[1] K. Fukuda, I. Maki, S. Ito, Remelting reaction within belite crystals during cooling, J. Am. Ceram. Soc. 75 (10) (1992) 2896–2898.
[2] K. Fukuda, I. Maki, S. Ikeda, S. Ito, Microtextures formed by the remelting reaction in belite crystals, J. Am. Ceram. Soc. 76 (11) (1993) 2942–2944.
[3] K. Fukuda, I. Maki, S. Ito, H. Yoshida, C. Kato, Effect of Al/Fe ratio in belite on the microtexture induced by the remelting reaction, J. Am. Ceram. Soc. 77 (11) (1994) 3027–3029.
[4] K. Fukuda, I. Maki, S. Ito, K. Toyoda, Kinetics of remelting reaction in Ca_2SiO_4 solid solutions, J. Ceram. Soc. Jpn. 103 (5) (1995) 444–448.
[5] K. Fukuda, I. Maki, S. Ito, H. Yoshida, Phase stability study on the remelting reaction in Ca_2SiO_4 solid solutions, J. Am. Ceram. Soc. 78 (12) (1995) 3387–3389.
[6] K. Fukuda, I. Maki, S. Ito, Transformation-induced microtextures in belite, Proceedings of 10th International Congress on the Chemistry of Cement, Sweden, 1997, Amarkai and Congers Goteborg, Goteborg, Sweden, 1997, p. 1i52.
[7] K. Fukuda, I. Maki, Orientation of β-Ca_2SiO_4 solid solution lamellae formed in the host α-phase, Cem. Concr. Res. 19 (6) (1989) 913–918.

[8] K. Fukuda, I. Maki, Orientation of coherent interphase boundaries formed by the α to α'_H phase transition in belite crystals, Cem. Concr. Res. 23 (3) (1993) 599–602.

[9] K. Fukuda, Redetermination of orientation of coherent interface boundaries between α- and α'_H-phases in dicalcium silicate, Cem. Concr. Res. 28 (8) (1998) 1105–1108.

[10] K. Fukuda, S. Ito, Highly reactive remelted belite, J. Am. Ceram. Soc. 82 (3) (1999) 637–640.

[11] K. Fukuda, S. Ito, Improvement in reactivity and grindability of belite-rich cement by remelting reaction, J. Am. Ceram. Soc. 82 (8) (1999) 2177–2180.

[12] K. Fukuda, N. Wakamatsu, S. Ito, H. Yoshida, Acceleration of early hydration in belite-rich cement by remelting reaction, J. Ceram. Soc. Jpn. 107 (10) (1999) 901–906.

[13] G.W. Groves, Twinning in β-dicalcium silicate, Cem. Concr. Res. 12 (5) (1982) 619–624.

[14] Y.J. Kim, I. Nettleship, W.M. Kriven, Phase transformations in dicalcium silicate: II. TEM studies of crystallography, microstructure, and mechanisms, J. Am. Ceram. Soc. 75 (9) (1992) 2407–2419.

[15] H.F.W. Taylor, Cement chemistry, Academic Press, New York, 1990.

[16] K. Fukuda, I. Maki, K. Toyoda, S. Ito, Kinetics of the α-to-α'_H polymorphic phase transition of Ca_2SiO_4 solid solutions, J. Am. Ceram. Soc. 76 (7) (1993) 1821–1824.

[17] E.F. Osborn, A. Muan, Fig. 630 in phase diagrams for ceramists, in: M.K. Reser (Ed.), Phase diagrams for ceramists, American Ceramic Society, Columbus, OH, 1964, p. 219.