Pergamon

Cement and Concrete Research, Vol. 27, No. 7, pp. 989–993, 1997
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0008-8846/97 $17.00 + .00

PII S0008-8846(97)00085-9

ACTIVITY OF β-C_2S UNDER DIFFERENT SINTERING CONDITIONS

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(Communicated by D. M. Roy)
(Received October 3, 1996; in final form April 23, 1997)

ABSTRACT

This paper describes a study undertaken to examine the crystal size, crystal internal micro-stress, specific surface of pores, and hydration rate of β-C_2S under rapid sintering (800°C/min) and normal sintering (25°C/min) conditions. The test results show that, under rapid sintering, the formed β-C_2S has finer crystal size, higher internal micro-stress, larger specific surface of pores, and thus higher rate of hydration. © *1997 Elsevier Science Ltd*

Introduction

Low hydration rate of β-C_2S hinders its application. For the purpose of production of β-C_2S cement, more and more attention was paid to improve its activity. Up to now, the measures having been taken include to form β-C_2S solution by the addition of trace elements (1,2), or to synthesize β-C_2S by autoclaving and then low temperature sintering (3), or to form it by low temperature sintering (1). The aim of this study is to investigate the activity of β-C_2S under rapid sintering (800°C/min) and normal sintering (25°C/min) conditions.

Experimental

The raw mix was made of $CaCO_3$ and silica with analytical purity and fineness of totally passing through 0.080mm and 0.054mm sieve size respectively. The mole ratio of $CaCO_3$/silica is 2.0. B_2O_3 0.01 mole with a fineness of totally passing through 0.080mm sieve size was added as stabilizer. After thoroughly mixing, the raw mix was mixed with small amount of distilled water and then was pressed at pressure of 60 MPa to get $\phi 15 \times 1$mm specimens. Then the specimens were dried at 105°C to constant weight and stored for experiment.

The sintering conditions adopted in this study and the f-CaO content under those conditions are shown in Table 1. The designed parameters include sintering rate, sintering temperature, and the length of temperature conservation.

Results and Discussion

Crystal Size and Micro-stress. The magnitude of free energy or the degree of deformation of crystal can be expressed by its internal micro-stress. The measurement of internal micro-

TABLE 1

Sintering Condition of β-C_2S

No.	F1	F2	F3	S
Sintering rate(℃/min)	800	800	800	25
Sintering temperature(℃)	1400	1450	1400	1400
Length of temperature conservation(min)	20	20	45	720
f-CaO (wt.%)	0.36	0.01	0.01	0.36

stress is based on the x-ray diffraction. When x-rays penetrate into a crystal and correspond to the Bragg equation $2d\sin\theta = n\lambda$, diffraction of the x-ray beam takes place. For a given λ, there is only a θ value corresponding to a d value, i.e., the diffraction peak should be a very sharp one. Actually, the diffraction peaks obtained always have a finite width. There two reasons for the widening of diffraction peaks. One is called the geometry widening which is caused by the different sizes and shapes of specimens and the divergence of x-rays. Another kind of widening, which called "real widening", is caused by the difference of fineness of crystal particles and the existence of inhomogeneous micro-stress in the crystals. The extent of widening can be expressed by the variance of diffraction patterns. Thus, after the relationship of internal micro-stress and microcrystal sizes with variance of diffraction patterns is found out, the inner micro-stress and microcrystal size can be obtained by the calculation of variance of diffraction patterns (4).

Since the circumstance of particles in the solid surface is different from that in the interior, the microstructure in the surface layer of a solid is also different from that in the interior. The surface exhibits a higher free energy, which leads to the polarization, deformation, and rearrangement of particles in the surface and thus the deformation of the crystal lattice. Crystal deformation produces an internal micro-stress. Lattice deformation is also due to the introduction of impurities and rapid change of temperature. A larger crystal surface energy produces a larger lattice deformation and thus the induced internal micro-stress. Also, a larger inner micro-stress leads to a higher free energy of crystal and thus the hydration activity of crystal (2). The measured internal micro-stress and particle size of β-C_2S crystal are shown in Table 2.

From Table 2 we can see that, with the same sintering temperature, the formed β-C_2S crystal particle size under rapid sintering (F1) is smaller than under normal sintering (S). The later is 2.5 times over the former. Prolonged sintering time and higher sintering temperature also produce a larger crystal particle size (F3 > F1, F2 > F1). The internal micro-stress of specimen F1 is larger than that of S, as well as than that of F2 and F3. The test results described above imply that the activity of β-C_2S formed under rapid sintering is higher than that formed under normal sintering. For the same rate temperature rise, the activity of the

TABLE 2

Particle Sizes and Inner Micro-stress of β-C_2S Crystal

NO.	F1	F2	F3	S
Particle size(Å)	476	699	986	1199
Internal micro-stress(ε^2)	1.94×10^{-3}	1.22×10^{-3}	1.18×10^{-3}	1.13×10^{-3}

TABLE 3

Pore Size Distribution of β-C_2S

pore radius (Å)	cumulative distribution of pore volume(cm^3/g × 10^{-3})		cumulative distribution of specific surface of pore			
			F1		S	
	F1	S	m^2/g × 10^{-2}	%	m^2/g × 10^{-2}	%
600~450	0.602	2.772	4.8	4.78	23.1	32.86
450~300	1.595	3.576	15.2	15.12	31.6	44.96
300~200	2.104	3.874	23.4	23.28	36.4	51.78
200~100	2.541	4.041	35.3	35.12	40.9	58.18
100~50	2.806	4.115	49.8	49.55	47.1	67.00
50~20	3.194	4.319	100.5	100.00	70.3	100.00

β-C_2S formed decreases as the sintering temperature increases. Prolonged sintering time makes the β-C_2S less activity.

Pore Distributions of β-C_2S. Pore distribution of β-C_2S is measured by DIGISORB 2600V4.0 microcrystal instrument and is shown in Table 3.

Table 3 shows that the total pore volume of F1 (3.194×10^{-3} cm^3/g) is smaller than that of S (4.319×10^{-3} cm^3/g) whilst the specific surface of pores of the former (100.5×10^{-2} m^2/g) is larger than that of the later (70.3×10^{-2} m^2/g), implying that the number of pores of F1 is larger than that of S. From Table 3 it also can be seen that, for specimen F1, the percentage of specific surface of pores for the pores smaller than 100Å is 64.88%, whilst for the specimen of S, the value is 41.92%. Thus it can be concluded from mentioned above that a looser microstructure of β-C_2S is formed under rapid sintering, which is beneficial for the improvement of activity of β-C_2S.

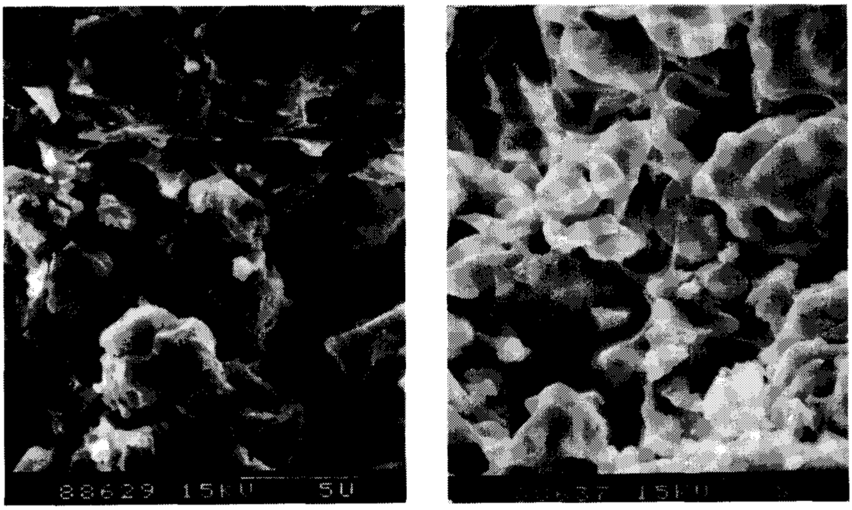

FIG. 1.
SEM images of β-C_2S.

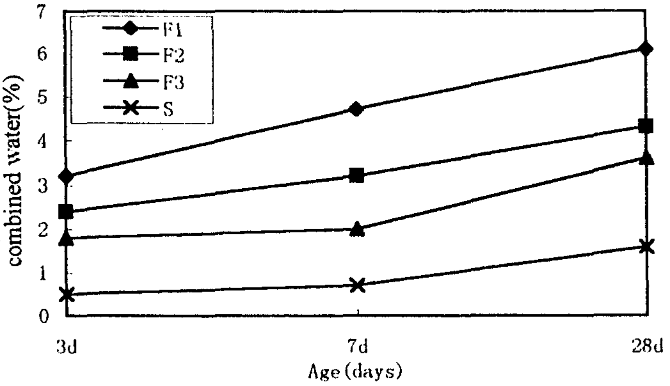

FIG. 2.
Combined water of β-C_2S under different sintering conditions.

SEM Images of β-C_2S. Fig. 1 shows the SEM images of F1 and S. It can be seen that crystal surface of β-C_2S under rapid sintering (F1) is rougher. There are more micropores and fissures in the crystal. For the β-C_2S under normal sintering (S) however, the crystal surface is smooth and no fissures can be found. These also imply that the activity of β-C_2S under rapid sintering is higher than that under normal sintering.

Hydration Rates of β-C_2S. Fig. 2 shows that the measured combined water of specimens cured at temperature of 20 ± 3°C and different ages. The sequence of quantity of combined water from larger to smaller is F1 > F2 > F3 > S, which corresponds to the values of internal micro-stresses (e^2), the values of crystal particle sizes as well as the values of specific surface of pores, pore size distribution and crystal appearances. That is, the smaller crystal particle size, the larger internal micro-stress, the larger specific surface of pores will create higher hydration rate of β-C_2S. Hydration rate of β-C_2S under rapid sintering is higher than that under normal sintering. In the case of rapid sintering, when the sintering temperature keeps constant, the hydration rate of β-C_2S decreases as the temperature conservation time increases (F1, F3). When the length of temperature conservation is kept constant, the hydration rate of β-C_2S decreases as the sintering temperature increases.

Conclusions

1. The formed β-C_2S under rapid sintering has higher specific surface of pores, smaller crystal particle size, more crystal defects, larger inner micro-stress, and thus higher hydration activity.
2. In the case of rapid sintering, when the sintering temperature is kept constant, the hydration activity of β-C_2S decreases as the temperature conservation time increases because of the formation of larger crystal size and smaller inner micro-stress. When the sintering temperature is kept constant, the hydration activity of β-C_2S decreases as the temperature conservation time increases, for the same reasons.

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