SHORT COMMUNICATIONS

On the Influence of Sodium Oxide upon the Crystal Structure of Tricalcium Silicate

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The crystal structure of pure $3CaO\cdot SiO_2$ and the solid solution of the system $3CaO\cdot SiO_2$-Al_2O_3-MgO, so-called alite, had been determined[1,2]. No results, however, had been reported on the influence of Na_2O upon $3CaO\cdot SiO_2$ and there existed a need for detailed investigation on this system.

In the present paper, the authors describe the results of the investigation on the formation and decomposition of the solid solution of the system $3CaO\cdot SiO_2$-Na_2O and its crystal structure.

Pure $3CaO\cdot SiO_2$ was synthesized by following procedures, that is, the mixtures of alkali free guaranteed reagent of $CaCO_3$ and SiO_2 were heated in platinum crucible at 1500°C, then cooled rapidly, pulverized, reheated several times until no free CaO was found. Then various amount of guaranteed reagent of $Na_2\cdot CO_3$ were added to $3CaO\cdot SiO_2$ and mixed sufficiently, heated at 1450°C for 30 min. and then cooled rapidly to room temperature.

This procedure was necessary to obtain the well-crystallized $3CaO\cdot SiO_2$-Na_2O solid solution. Chemical compositions, refractive indices and specific gravity of the solid solution of this system are shown in Table I.

X-Ray diffraction pattens of the characteristic peaks at $51\sim52$°C in 2θ corresponding to (220) of Jeffery's trigonal cell[1,2] of the $3CaO\cdot SiO_2$-Na_2O solid solution measured by slow scanning and high resolution are shown in Fig. 1.

These characteristic peaks were triplet until Na_2O content increased to 0.33% and then changed to doublet. Further increase of a Na_2O content made no remarkable change of the X-ray diffraction patterns of the $3CaO\cdot SiO_2$-Na_2O solid solution until 0.71%. More further addition of Na_2CO_3 decomposed it into β-$2CaO\cdot SiO_2$, $Na_2O\cdot CaO\cdot SiO_2$ and free CaO.

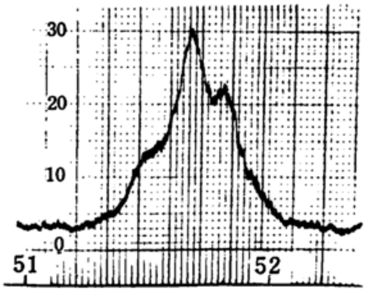

Fig. 1. X-Ray diffraction pattern of the characteristic peak of $3CaO\cdot SiO_2$-Na_2O solid solution (specimen No. 6).

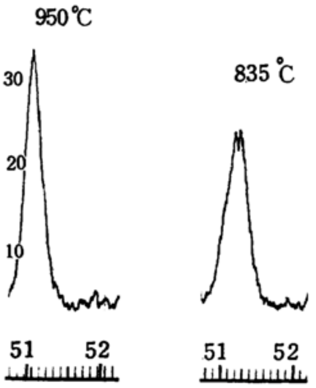

Fig. 2. High temperature X-ray diffraction patterns of the solid solution of the system $3CaO\cdot SiO_2$-Na_2O (specimen No. 6).

The triplet $\rightleftarrows$ doublet change seemed corresponding to triclinic $\rightleftarrows$ monoclinic transition.

In differential thermal analysis, the low Na_2O samples showed two endothermic and exothermic peaks at $900\sim1000$°C corresponding to the reversible transitions of triclinic $\rightleftarrows$ monoclinic $\rightleftarrows$ trigonal, but the high Na_2O ($0.3\sim0.7$% of Na_2O) samples showed one endothermic and exothermic peak of the monoclinic $\rightleftarrows$ trigonal transition.

In high temperature X-ray diffraction, doublet peaks of the high Na_2O sample changed to singlet at about 900°C as shown in Fig. 2.

From the results of X-ray diffraction and differential thermal analysis, the high Na_2O solid solution was considered to be monoclinic structure. Assuming that this solid solution have Yamaguchi and Miyabe's monoclinic cell[2] corresponding to pseudo-orthorhombic cell

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[1] J. W. Jeffery, *Acta Cryst.*, **5**, 26 (1952).

[2] G. Yamaguchi and H. Miyabe, *J. Am. Ceram. Soc.*, **43**, 219 (1960).

TABLE I. CHEMICAL COMPOSITION, REFRACTIVE INDICES AND SPECIFIC GRAVITY OF SYNTHESIZED PURE $3CaO\cdot SiO_2$ AND THE SOLID SOLUTION OF THE SYSTEM $3CaO\cdot SiO_2$-Na_2O

	Notation of specimen	SiO_2	CaO	Na_2O	Total	F. CaO	Sp. gr.	Refractive Indices	
								α	γ
Pure $3CaO\cdot SiO_2$		26.14	73.85	—	99.99	0.00	3.149	1.718±0.002	1.723±0.002
$3CaO\cdot SiO_2$-Na_2O solid solution	No. 1	26.13	73.81	0.05	99.99	0.12	—	—	—
	No. 2	26.10	73.74	0.14	99.98	0.34	—	—	—
	No. 3	26.08	73.67	0.25	100.00	0.73	—	—	—
	No. 4	26.05	73.61	0.33	99.99	0.85	—	1.717±0.002	1.721±0.002
	No. 5	26.02	73.50	0.48	100.00	1.36	—	1.716±0.002	1.720±0.002
	No. 6	25.97	73.34	0.71	100.02	2.92	—	1.715±0.002	1.718±0.002

derived from Jeffery's trigonal cell[1], lattice constants were determined by precise X-ray diffraction as follows:

$a=12.262$ a. u., $b=7.053$ a. u., $c=25.086$ a. u., $\beta=90^\circ 07'$.

Calculated value of interplaner spacing from these lattice constants coinside with those obtained by the precise measurement of the diffraction peaks.

By heating for three hours at 1450°C, the monoclinic high Na_2O solid solution released Na_2O and changed into the triclinic low Na_2O solid solution.

The gradual decomposition of $3CaO\cdot SiO_2$ into $2CaO\cdot SiO_2$ and free CaO occurred at about 1250°C was fairly accelerated in the solid solution, compared with that of pure $3CaO\cdot SiO_2$.

The rate of hydration of the solid solution was larger than that of pure $3CaO\cdot SiO_2$.

This solid solution seems significant because alite in commercial portland cement clinker contains a few amount of Na_2O and effect of Na_2O can not be little.

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