In-situ Phase Identification of Crystallized Compound from $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ Liquid

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In dephosphorization process in steelmaking, phosphorus in molten iron is distributed into molten slag after oxidized, and it forms $3\text{CaO}\cdot\text{P}_2\text{O}_5$. It has been known that dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) formed in molten slag and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ make a solid solution, which could promote dephosphorization efficiency from molten iron. It has been reported that $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution (α phase) is formed for entire composition range at higher temperatures than 1 673 K, and many previous studies on dephosphorization behavior assumed that the α phase would be precipitated from molten slag. However, we found that the α phase cannot be obtained at low phosphorus concentrations when the pellet of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ powders mixture is annealed and quenched to room temperature. In this study, we conduct high temperature *in-situ* X-ray diffraction analysis to the aerodynamically levitated sphere of the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ liquid to identify primary crystallized phase. It has been verified that the α phase is precipitated from the liquid for wide phosphorus concentrations. In addition, a rapid phase transition of the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution has been detected by the time-division X-ray diffraction with high resolutions when the levitated sample containing the α phase is quenched from the precipitated temperature.

KEY WORDS: dephosphorization; $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution; high temperature *in-situ* X-ray diffraction; aerodynamic levitation; crystallization.

1. Introduction

In Japanese steelmaking process, a large amount of phosphorus has been removed from molten iron by dephosphorization¹⁾ to prevent low temperature embrittlement of the solidified steel. The dephosphorization process is mainly performed with the dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, C2S) –saturated molten slag, and phosphorus behavior during the dephosphorization has been investigated by many authors.^{2–15)} Generally, phosphorus in molten iron is oxidized to P_2O_5 and preferentially distributed into molten slag, which forms the tri-calcium phosphate ($3\text{CaO}\cdot\text{P}_2\text{O}_5$, C3P) compound in the slag. On the other hand, as lime for the refining agent is dissolved to the molten slag, dicalcium silicate compound is spontaneously precipitated in the slag. It has been known that the $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ form a solid solution, and that the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ solid solution in molten slag plays a significant role to enhance the dephosphorization efficiency from molten iron.^{6–8)} Therefore, it is important to determine the phosphorus solubility in the dicalcium silicate compound precipitated in the molten slag.

According to the phase diagram of the $2\text{CaO}\cdot\text{SiO}_2\text{--}$

$3\text{CaO}\cdot\text{P}_2\text{O}_5$ pseudo-binary system, it has been reported that $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ form a solid solution at the entire composition range (α phase) in the temperature above 1 673 K.^{16,17)} As example, the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ phase diagram reported by Fix *et al.*¹⁷⁾ is shown in Fig. 1. The reported C2S–C3P phase diagram shows very unique phase relationship: the α phase is recognized as the primary precipitated phase from liquid phase in the entire composition range. In contrast, in the low phosphorus composition range (0–20 mass% C3P) in this diagram, the α phase solid solution is transformed into the α' phase at 1 319 K–1 693

Fig. 1. The pseudo-binary phase diagram of the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$ system reported by Fix *et al.*¹⁷⁾

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K according to the upper boundary of α and α' phase coexistence area and the β phase at temperatures less than 943 K, which show the limited phosphorus solubility. In the composition range of 20–50 mass% C3P, alternatively, the α phase is decomposed into the intermediate compound $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$ (“A” in Fig. 1) and the α' -C2S solid solution. Thus, in the reported C2S-C3P phase diagram, many kinds of intermediate compounds are found at low temperatures, while only the α phase is recognized in the whole composition range at high temperatures.

Many previous dephosphorization studies^{2–15)} assumed that the α phase of the C2S-C3P solid solution is precipitated in molten steelmaking slag. However, since molten steelmaking slag is multi-component oxide system including FeO and MgO which could be dissolved into the dicalcium silicate, it has not been clear whether the α phase of the C2S-C3P solid solution is precipitated. At present, there are no evidences to verify the α phase formation in molten slag.

To verify the formation of the α phase solid solution in the C2S-C3P system at high temperatures, we conducted the preliminary tests by the following way: first, the mixture of γ -2CaO·SiO₂ and β -3CaO·P₂O₅ powders at different C3P contents (5, 10, 20 and 35 mass% C3P) was compacted into a pellet of 10 mm in diameter and 5 mm in height. Second, the mixture pellet was annealed at 1 873 K for 18 h in air atmosphere, and then quenched by pressing it with two thick Cu plates (150 mm in diameter and 30 mm in thickness). In this case, the cooling rate of $-200 \text{ K} \cdot \text{s}^{-1}$ was expected. Then, the cooled sample was crashed into the powder. We repeated the above procedures for more than 3 times to promote solid state reaction between 2CaO·SiO₂ and 3CaO·P₂O₅ particles. Third, the existing crystalline phases were identified in the annealed sample by the powder X-ray diffraction analysis at room temperature by a Rigaku RINT 2500 diffractometer using Cu K α radiation and operating at 40 kV and 200 mA.

Figure 2 shows the results of the powder X-ray diffraction analysis of the annealed samples of the C2S-C3P system. For the C2S – 35 mass% C3P sample, the very simple diffraction pattern corresponding to the α phase¹⁸⁾ was observed. For the C2S – 5, 10, 20 mass% C3P samples, however, the obtained diffraction patterns were complicated, which corresponded to the α' or β phases of C2S compound^{19,20)} rather than the α phase. Therefore, the α phase solid solution was not verified for the lower C3P content than 35 mass% in the C2S-C3P system, whereas other crystalline phases were alternatively observed. The result of the above preliminary test suggested that either phase relationship in the C2S-C3P system at high temperatures need to be re-evaluated, or a very rapid phase transition from the α phase to the α' or β phases is assumed to occur during quenching the annealed sample.

As pointed previously, it should be noted that the C2S-C3P phase diagram reported by Fix *et al.*¹⁷⁾ indicates that the α solid solution is the primary crystal phase precipitated from the liquid phase for the whole composition range. For verification of the α phase formation, it should be the appropriate way to prepare the liquid phase in the C2S-C3P system and identify the primary crystallized phase by high temperature *in-situ* structural analysis because each oxide component is decomposed into ions which are completely

Fig. 2. X-ray diffraction patterns of the 2CaO·SiO₂–3CaO·P₂O₅ solid solution samples after repeating the annealing at 1 873 K for 20 h and quenching with Cu plates for 3 times ($\lambda = 1.5418 \text{ \AA}$, C2S = 2CaO·SiO₂, C3P = 3CaO·P₂O₅). (Online version in color.)

mixed in the liquid phase. However, it is difficult to raise up the temperature higher than 2 273 K for liquid phase formation in the C2S-C3P system, in terms of materials for liquid container and heating element.

On the other hand, the aerodynamic levitation technique with laser heating has been established recently to prepare high temperature melt sphere without any container, and applied for the evaluation of some physical properties^{21–25)} as well as the microscopic structure analysis of high temperature melt by combining with high energy X-ray or neutron radiation.^{26–38)} In addition, time resolved diffraction measurement is even available by use of high energy X-ray provided in the SPring-8 synchrotron radiation center, which has enabled the crystallization behavior from molten state to be detected *in-situ* with a high resolution.^{37,38)} However, the reported examples that applied the above technique to analyze the dynamic phase transition behavior are limited to unary material so far, and no trials has not been done for mixed oxide systems or even multi-component slag.

In the present study, we have applied the above aerodynamic levitation technique coupled with high energy X-ray radiation to conduct *in-situ* high temperature XRD analysis of the precipitated compound phase from the melt of the 2CaO·SiO₂–3CaO·P₂O₅ pseudo-binary system to verify the α phase formation as the primary crystallized phase. In addition, time-division X-ray diffraction has been applied to track a rapid phase transition behavior of the 2CaO·SiO₂–3CaO·P₂O₅ solid solution when quenched from the precipitated temperature.

2. Experimental Procedure

We prepared the 2CaO·SiO₂–3CaO·P₂O₅ (C2S-C3P) solid solution samples by mixing γ -2CaO·SiO₂ and β -3CaO·P₂O₅ powders, pressing the mixture into a pellet, and annealing

the pellet at 1 873 K for 12 h in air. The C3P content was varied among 5, 10, 20, and 35 mass%. Then, the sample was crashed into a piece with 2 mm in diameter, and set to the nozzle for the aerodynamic levitation apparatus originally installed in BL04B2 beamline in SPring-8. The schematic diagram of the aerodynamic levitation apparatus is shown in **Fig. 3**: the sample was levitated by highly-pure Ar gas (99.9996% in purity) jet stream from the bottom of the nozzle (gas inlet size: 1.0 mm in diameter) made by copper. The CO₂ gas laser was generated by a Synrad Firestar t-100 laser oscillator with 10.6 μm in laser wavelength, 2.2 mm in laser diameter and 100 W in average output power, and irradiated the levitated sample from up above through a reflecting mirror and a collecting lens, heating the sample up to 2 673 K for complete melting. **Figure 4** shows an example of captured picture of the levitated C2S sample in the molten state. The sample temperature was measured by a pyrometer, where the calibration was performed so as to reproduce the crystallization temperatures of alumina (2 346 K) and pure C2S (2 413 K) as reference materials. It should be noted that the levitated melt sphere is easily supercooled without nucleation.^{22,26–29,39–42)} To promote the crystallization below the melting point, we added 1 mass% Pt powder as nucleation agency to the reference materials. We detected the recalescence phenomenon in the temperature profile recognized as the crystallization. However, the recorded temperature should be originally calibrated by the emissivity of each treated sample including its composition and temperature dependences. As the first approximation, we assumed that the emissivity of C2S-C3P melt is similar

Fig. 3. Experimental apparatus for X-ray analysis of the aerodynamically levitated sample.

Fig. 4. Captured picture of levitated molten 2CaO·SiO₂ sample.

to those of the reference materials regardless of the C3P content and temperature.

In this study, the above levitating apparatus was installed in BL08W in SPring-8 to combine with high energy coherent X-ray (115.6 keV) light source achieved by use of superconducting wiggler. This enables the diffraction patterns to be obtained with wide ranges of scattering vector ($q = 4\pi\sin\theta/\lambda$, θ : diffraction angle, λ : wavelength), which is useful for evaluating ionic arrangements after Fourier transformation. In addition, the use of high energy coherent X-ray enables time resolved diffraction measurement to be done with high resolutions.³⁸⁾ The high energy X-ray was radiated to the levitated molten sample, and the diffracted light together with transmitted light were transferred to a two-dimensional Si flat panel detector with 1.5 s intervals. The X-ray beam size was 3 mm in height and 1 mm in width, therefore X-ray was radiated throughout much of the levitated sample. The beam center position and the camera distance were determined using the obtained diffraction pattern of the CeO₂ reference material. The obtained two-dimensional area-detector image were reduced to one-dimensional patterns through the Orochi (PIXIA) software developed by Dr. Satoshi Tominaka in National Institute for Materials Science, Japan.

The chemical compositions of the samples after the experiment were analyzed by the energy dispersion spectroscopy, resulting in the verification that the Ca/Si/P composition ratio of each sample corresponded to the designed composition.

3. Results and Discussion

3.1. Primary Crystallized Phase Identification of 2CaO·SiO₂–3CaO·P₂O₅ Melt

Figures 5 and 6 represent an example of temperature profile and two-dimensional area-detector image when the crystallization occurred from the C2S-5 mass% C3P melt with no nucleation agent. The moments when images (a)–(c) in **Fig. 6** were collected are represented in **Fig. 5**. Although the liquidus temperature was reported as above 2 373 K,^{16,17)} the levitated melt was supercooled over 400 K and the actual crystallization occurred at around 1 968 K. Once the crystallization occurred, temperature raised up only in a moment

Fig. 5. Temperature profile for crystallization of 2CaO·SiO₂–5 mass% 3CaO·P₂O₅ sample from liquid state: (a) liquid state, (b) α phase precipitation, (c) crystallization completed.

due to latent heat generation (Fig. 5). The area-detector image of the melt before the crystallization (Fig. 6(a)) represented the halo pattern, whereas after the precipitation (Fig. 6(b)) several diffraction spots showing their rotation trajectories were observed, all of which indicated the precipitation of the α -C2S crystal as the one-dimensional diffraction pattern corresponded to that reported by Mumme *et al.*¹⁸⁾ In a few seconds after the precipitation (Fig. 6(c)), only several diffraction spots and the diffuse scattering were observed in the area-detector image. The comparison between the observed two-dimensional diffraction image of the crystallized compound and the calculated diffraction image of the α -C2S single crystal according to the crystal structure by Mumme *et al.*¹⁸⁾ is shown in Fig. 7, which demonstrates that all of the observed diffraction spots well agreed with the diffraction of the α -C2S single crystal from a [010] single orientation. Therefore, it was concluded that the sample was crystallized to form the single crystal of α phase. In contrast, the diffuse scattering observed along [100] orientation may contain the contributions from the disordered atomic arrangement in the precipitated α phase crystal.

Figure 8 represents the observed two-dimensional diffraction images after the crystallization occurred from C2S-C3P melt of different compositions. At low phosphorus compositions (Figs. 8(a)–8(c)), where [100] and [001] crystal zone axes are also drawn, the observed diffraction spots were recognized as the single crystal of α phase. The

formation of single crystal from the C2S-C3P melt was probably due to the significant degrees of supercooling, which can make large driving forces of crystallization. In contrast, the detected image from the C2S-35 mass% C3P composition (Fig. 8(d)) exhibited several ordered trajectories showing Debye-Scherrer rings, indicating the formation of polycrystalline compound of α phase.

Figure 9 shows the one-dimensional diffraction patterns of the polycrystalline phase obtained from the C2S-C3P samples with varied C3P contents, after cooled to room temperature and reheated at higher temperatures than 1 973 K. The calculated diffraction peak positions for pure α -C2S crystal at 1 818 K based on the report by Mumme *et al.*¹⁸⁾ are also shown by dashed lines for comparison. It was confirmed that the crystalline phase corresponded with the α -C2S phase regardless of C3P content in the sample. However, several diffraction peaks were split and the peak positions were slightly deviated between each sample. The resolution of two-dimensional diffraction detection may have partially affected the deviations. However, this probably indicated that the ionic arrangement is disordered to some extents in the precipitated α phase crystal at high temperatures. Nevertheless, the above result on primary phase identification was in agreement with the reported phase diagram of the C2S-C3P system,¹⁷⁾ although the liquidus and solidus temperatures were not able to determine due to the sample supercooling.

Fig. 6. Two-dimensional area-detector images when crystallization of 2CaO·SiO₂–5 mass% 3CaO·P₂O₅ sample occurred from the liquid state. (Online version in color.)

Fig. 7. Comparison between (a) observed two-dimensional diffraction image of precipitated crystal from 2CaO·SiO₂–5 mass% 3CaO·P₂O₅ liquid, and (b) calculated α -2CaO·SiO₂ single crystal diffraction image along [010] orientation according to crystal structure proposed by Mumme *et al.*¹⁸⁾ In Fig. 7(b), red dots and dashed lines describe diffraction spots and diffuse scattering patterns observed in Fig. 7(a). (Online version in color.)

Fig. 8. Observed two-dimensional diffraction images of precipitated crystal from different compositions of $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ liquid, where $[100]$ and $[001]$ crystal zone axes are drawn as red lines. (Online version in color.)

Fig. 9. One-dimensional *in-situ* X-ray diffraction patterns of polycrystalline compound obtained from $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ samples reheated at higher temperatures than 1 973 K. ($\lambda = 0.1072\text{Å}$, $\text{C2S} = 2\text{CaO}\cdot\text{SiO}_2$, $\text{C3P} = 3\text{CaO}\cdot\text{P}_2\text{O}_5$).

However, the above result was inconsistent with our preliminary experimental result, where other crystalline phases than the α phase were obtained for the annealed and quenched C2S-C3P solid samples with low phosphorus

contents. The possible explanation was that the rapid phase transition occurred during quenching the annealed C2S-C3P solid sample, which we particularly investigated in the next section.

3.2. Rapid Phase Transition of $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ Solid Solution in Quenching

To identify the rapid phase transition of the α C2S-C3P solid solution phase, we conducted time-resolved *in-situ* X-ray diffraction of the C2S-C3P sample in quenching after the α phase precipitation. **Figures 10 and 11** show an example of the obtained area-detector images during the quench of the C2S-5 mass% C3P sample. As the laser heating was stopped, the sample at a high temperature was suddenly cooled down and the temperature reached less than 1 123 K (the lower-limit detectable by the pyrometer) in a second. The cooling rate was estimated as in the order of $-1\,000\text{ K}\cdot\text{s}^{-1}$. In spite of such a rapid cooling, the detector images at 1.5 s intervals (Figs. 11(a)–11(c)) suddenly changed to demonstrate the phase transition from the single crystal α phase to the polycrystalline β phase. Thus, the rapid phase transition was successfully detected for the C2S-5 mass% C3P composition by the time-resolved X-ray diffraction.

Figure 12 represents the results of one-dimensional diffraction patterns of the C2S-C3P sample of varied C3P contents, after quenched from the α phase at higher temperatures than 2 073 K. For the composition range of 5–20 mass% C3P, the diffraction patterns of the quenched samples were clearly different from those before being quenched (α phase), demonstrating the presence of the β and α' phases for the C2S-10, 20 mass% C3P compositions, whereas only the β phase formation in the C2S-5 mass% C3P composition

Fig. 11. Two-dimensional area-detector images when $2\text{CaO}\cdot\text{SiO}_2$ –5 mass% $3\text{CaO}\cdot\text{P}_2\text{O}_5$ sample was quenched after the α phase precipitation. (Online version in color.)

Fig. 10. Temperature profile for quenching of $2\text{CaO}\cdot\text{SiO}_2$ –5 mass% $3\text{CaO}\cdot\text{P}_2\text{O}_5$ sample after α phase precipitation: (a) initial of being quenched (α phase), (b) being quenched, (c) after quenched.

after quenched. For the C2S-35 mass% C3P composition, however, the α phase remained in the diffraction pattern after quenched, where the observed diffraction peak positions were slightly deviated from the reference by Mumme *et al.*¹⁸⁾ for pure α -C2S due to the C3P solubility in the obtained compound. This indicates that the rapid phase transition did not occur in the C2S-35 mass% C3P composition. The above result was in agreement with those from our preliminary test in terms of identified crystalline phases, where not the α phase but other solid solution phases were obtained for low phosphorus compositions when the powder mixture sample was annealed and then quenched.

Thus, we have confirmed that the $\alpha \rightarrow \alpha'$ or $\alpha' \rightarrow \beta$ phase transitions occur very rapidly in quenching the sample in the composition range of C2S – (5–20 mass%) C3P, although the α phase remains after quenched for the C2S-35 mass% C3P composition. Here, we discuss (i) the reason why the α solid solution phase was rapidly transformed into the α' phase in low phosphorus compositions, and (ii) the reason why, in contrast, the α phase remained after quenched for high phosphorus composition, in terms of similarity in the crystal structures among several solid solution phases.

Figure 13 shows the reported crystal structures of dicalcium silicate (C2S) compound.^{18,19,43–46)} The α phase, stable at high temperatures, exhibits a hexagonal crystal structure, where isolated Ca^{2+} and SiO_4^{4-} ions are distributed symmetrically. In contrast, the α' phase shows an orthorhombic crystal structure with asymmetric distributions of isolated

Fig. 12. One-dimensional X-ray diffraction patterns of $2\text{CaO}\cdot\text{SiO}_2$ –3CaO· P_2O_5 samples after quenched. ($\lambda = 0.1072\text{Å}$, C2S = $2\text{CaO}\cdot\text{SiO}_2$, C3P = $3\text{CaO}\cdot\text{P}_2\text{O}_5$). (Online version in color.)

Ca^{2+} and SiO_4^{4-} ions. The β phase, which is known as the metastable phase formed in cooling procedure of the α' phase,^{43,44)} represents a monoclinic crystal structure where distribution of Ca^{2+} and SiO_4^{4-} ions are asymmetric. According to the crystal structure of tri-calcium phosphate,⁴⁶⁾ where phosphorus forms PO_4^{3-} tetrahedron and is distributed alternately with Ca^{2+} ions, phosphorus is assumed to be incorporated into each C2S crystal structure by substituting two SiO_4^{4-} tetrahedrons with PO_4^{3-} tetrahedrons and making one vacancy in the first neighbor Ca^{2+} site, which would not change much the crystallography of the dicalcium silicate mother phases.

As shown in Fig. 13, similarity is clearly found in the distribution relationship between Ca^{2+} and SiO_4^{4-} ions in each crystal structure of dicalcium silicate: that is to say, a layer of each one Ca^{2+} and one SiO_4^{4-} alternately distributed (named as Ca-T layer), and the other layer of Ca^{2+} ions successively placed (named as Ca layer), are commonly found along c-axis in α -C2S, a-axis in α' -C2S, and b-axis in β -C2S, respectively. Therefore, as pointed by several

Fig. 13. Crystal structures of dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, C2S): (a) α phase, (b) α' phase, (c) β phase.^{18–20} (Online version in color.)

authors in terms of C2S crystallography,^{42–45} the $\alpha \rightarrow \alpha'$ or $\alpha' \rightarrow \beta$ phase transitions are considered to occur by the displacement of Ca^{2+} and SiO_4^{4-} ions rather than general nucleation and growth mechanism. It should be noted that, in the composition range of C2S – (5–20 mass%) C3P in the reported C2S–C3P phase diagram,¹⁷ the $\alpha \rightarrow \alpha'$ or $\alpha' \rightarrow \beta$ phase transitions should occur at each transition temperature. Thus, for low phosphorus concentrations, the rapid phase transitions from α to α' and from α' to β were observed in quenching the corresponding samples at high temperatures.

For the C2S–35 mass% C3P composition, however, the reported C2S–C3P phase diagram¹⁷ indicates that the phase transition should occur from α to α' and A (Nagelschmidite, $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$) intermediate compound during the cooling of the α solid solution phase. The Nagelschmidite intermediate compound has been found as a solid solution in the $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5\text{--}2\text{CaO}\cdot\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ quaternary system, and its crystal structure has been investigated by several authors.^{48–51} Widmer *et al.*⁵¹ refined the crystal structure of Nagelschmidite previously reported by Celotti *et al.*⁴⁹ for $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$ end-member, however each atomic site position was not listed. **Figure 14** represents the crystal structure of the $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$ Nagelschmidite based on the reports by Celotti *et al.*⁴⁹ and Sugiyama *et al.*⁵⁰ for Si sites. It was reported⁵⁰ that Ca^{2+} vacancies due to substitution of PO_4^{3-} for SiO_4^{4-} are orderly distributed in the Ca–T layer to form the vacancy-tetrahedron layer, which corresponds to the ordered substitution of PO_4^{3-} for SiO_4^{4-} in the neighbour Ca–T layer. On the other hand, the distribution of SiO_4^{4-} or PO_4^{3-} tetrahedrons in the Ca–T layer in the α phase solid solution is not ordered. Therefore, it suggests that ionic diffusion is required for the phase transition from the α phase to the $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$ compound. This probably explains our result that the α phase remained without the $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$ compound formation in quenching the C2S–35 mass% C3P sample at a high temperature.

Finally, we shortly discuss the stability of the α phase structure at high temperatures and its high phosphorus solubility in the C2S–C3P system: although we verified that the α phase is recognized as the primary crystal phase precipitated from the liquid phase for wide C3P contents, (I) why

Fig. 14. Crystal structure of Nagelschmidite ($\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$) intermediate compound based on Celotti *et al.*,⁴⁹ where Si sites are estimated from report by Sugiyama *et al.*⁵⁰ (Online version in color.)

the α phase with the symmetric and immaculate distributions of Ca^{2+} and SiO_4^{4-} ions is found as the primary crystal, and (II) why the crystal structure of the α phase shows high phosphorus solubility, could not be clearly explained at this stage. In particular, we consider that it is very strange that the α phase is precipitated as the primary crystal from the liquid phase, although the configurational entropy of the α -dicalcium silicate crystal with ordered structure is apparently much lower than the α' or β phase with disordered ionic distribution. However, as shown in Fig. 9, the split diffraction peaks indicate that ionic arrangement may be disordered in the precipitated α phase crystals, which may increase entropy and thus stability of the α phase at high temperatures. Currently, we have been evaluating the stability of ionic distributions in the α -dicalcium silicate crystal at high temperatures and the stability of the α phase crystal structure when doping phosphate ions by first principle calculations, which will be presented in our next paper.

In addition, our final goal is to directly identify the crys-

tal structure of the primary precipitated phase from molten steelmaking slag, particularly to verify if the α C2S-C3P solid solution phase is crystallized from the molten slag or not. We have been currently trying to apply the present experimental method to the determination of the crystallized phase from molten multi-component slag based on the dephosphorization process, which will be also presented in our another paper.

4. Conclusions

To verify the α solid solution phase formation in the $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ system at high temperatures, the $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ single liquid phase was prepared by the aerodynamic levitation technique with laser heating, and *in-situ* X-ray diffraction analysis was conducted for identifying the primary crystal precipitated from the melt. The obtained results are summarized as the following:

- For treated phosphorus compositions ($2\text{CaO}\cdot\text{SiO}_2$ –(5–35 mass%) $3\text{CaO}\cdot\text{P}_2\text{O}_5$), the α phase was confirmed to be precipitated as a primary crystal from the liquid phase. However, the observed diffraction peaks were split or broad, which probably indicates that ionic arrangement is disordered in the precipitated α phase crystal.
- When $2\text{CaO}\cdot\text{SiO}_2$ – $3\text{CaO}\cdot\text{P}_2\text{O}_5$ sample was quenched from high temperatures after the α phase precipitated, the α phase remained at room temperature for the $2\text{CaO}\cdot\text{SiO}_2$ –35 mass% $3\text{CaO}\cdot\text{P}_2\text{O}_5$ composition. In contrast, the α phase was transformed very rapidly to the β or α' phase for the $2\text{CaO}\cdot\text{SiO}_2$ –(5–20 mass%) $3\text{CaO}\cdot\text{P}_2\text{O}_5$ compositions.

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