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The Reactions of Silicon Phosphate with Alkaline Earth Metal Oxides at High Temperatures[1)]

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Synopsis. The reactions of $Si_3(PO_4)_4$ with CaO and MgO at high temperatures up to 1150 °C yielded silicon phosphate glass, $Me_3(PO_4)_2$, $Me_2P_2O_7$, and α-cristobalite, depending on the temperature, the heating time, and the $MeO/Si_3(PO_4)_4$ molar ratio (Me: Ca and Mg). These reactions were found to proceed by means of the one-way diffusion of alkaline earth metal oxides into the $Si_3(PO_4)_4$ phase.

The synthesis of SiO_2–P_2O_5 compounds was carried out by Makart[2)] and Liebau *et al.*,[3)] who reported the formations of $Si_3(PO_4)_4$ (hexagonal), SiP_2O_7 (**1**) (hexagonal), SiP_2O_7 (**2**) (monoclinic), SiP_2O_7 (**3**) (tetragonal), and SiP_2O_7 (**4**) (cubic) in the reactions of various SiO_2 compounds with phosphoric acid. However, no information is at present available on the chemical properties of these silicon phosphates. The present authors[4)] have previously prepared silicon phosphates, such as $Si_3(PO_4)_4$, and SiP_2O_7 (**1**, **2**, **3**), by means of the calcination of silica gel impregnated with a small amount of phosphoric acid at temperatures up to 1000 °C; they have thus shown that these phosphates can be used as a satisfactory hardener for silicate adhesives. A kinetic study of the hydrolysis of $Si_3(PO_4)_4$ in aqueous alkaline solutions was also carried out in this connection.[1)] Besides being useful as hardeners of silicate adhesives, silicon phosphates can also be used as binders of various ceramic materials and as raw materials for the production of glass. In this study, we investigated the reaction behaviors of $Si_3(PO_4)_4$ with CaO and MgO at high temperatures.

Experimental

Materials. $Si_3(PO_4)_4$ was prepared by the method reported previously.[1)] The particles were all disk-shaped, 2.2 μm in diameter ×0.9 μm in height. The CaO and MgO were of extra pure grade and were used after calcination at 500 °C for 1 h.

Reactions in the Powder Mixtures. The mixtures of $Si_3(PO_4)_4$ and CaO or MgO were wet with acetone and thoroughly mixed for 30 min in an agate mortar. Then, parts of the powder mixture (0.5—1.5 g) were transferred to a platinum boat, and it was heated at 940 °C in an electric furnace in air. Other parts of the powder mixtures of both systems ($MeO/Si_3(PO_4)_4$ molar ratio=3) were also heated at high temperatures up to 1150 °C with a heating rate of 10 °C min^{-1} in air using a Rigaku Denki Thermoflex TG-DTA apparatus. The reaction products in the samples were determined by means of X-ray diffraction analysis, using a Rigaku Denki Geigerflex D-2F with Ni filtered Cu $K\alpha$ radiation, with 30 kV and 10 mA.

Reactions at the Contact Surface of One-paired Tablets. The diffusion couples, *i.e.*, one-paired tablets, were prepared by a method similar to that used by Kinoshita *et al.*;[5)] about 2 g of $Si_3(PO_4)_4$ powder was pressed into a tablet 10 mm in diameter under a pressure of 640 kg cm^{-2}. A platinum tape (0.1×0.4×10 mm) was placed on the surface of the $Si_3(PO_4)_4$ tablet as a marker. Then, about 2 g of CaO or MgO powder was placed on the tablet, and it was pressed again into a double-layered tablet. After drying over P_2O_5 at room temperature, the diffusion couples were heated at 940 °C for 72 h in a manner similar to that described above. After these diffusion couples had been removed from the furnace, they were separated into two tablets from the border of a platinum marker. The reaction products in the surface layers of the tablets were examined by means of X-ray diffractometry in both the intact-tablet and powdered state.

Results and Discussion

$Si_3(PO_4)_4$–CaO System. The X-ray diffraction patterns of the products obtained in the reaction of the $Si_3(PO_4)_4$–CaO system using the TG–DTA apparatus are shown in Fig. 1. In this system, the reaction occurred at about 850 °C to yield β-$Ca_3(PO_4)_2$ and β-$Ca_2P_2O_7$ as crystalline products. As the temperature increased, the fraction of β-$Ca_2P_2O_7$ increased and that of β-$Ca_3(PO_4)_2$ decreased. At 1150 °C, β-$Ca_2P_2O_7$ and α-cristobalite were crystalline products. The X-ray diffraction lines of all the products were, on the whole, low, and a slight halation was observed in the X-ray diffraction pattern of 2θ=17—25° at 1150 °C. This means that an X-ray amorphous product such as silicon phosphate glass would be formed together with these crystalline products. In this system, no formation of crystalline

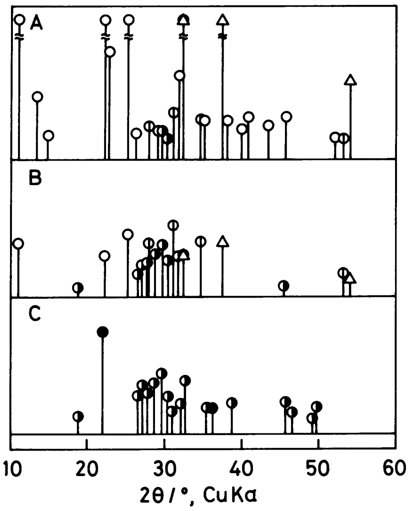

Fig. 1. X-Ray powder diffraction patterns of the mixture of $Si_3(PO_4)_4$–CaO (1 : 3) at the constant rate of heating (10 °C min^{-1}).
○: $Si_3(PO_4)_4$, △: CaO, ⦶: β-$Ca_3(PO_4)_2$, ◑: β-$Ca_2P_2O_7$, ●: SiO_2(α-cristobalite).
A: 850 °C, B: 950 °C, C: 1150 °C.

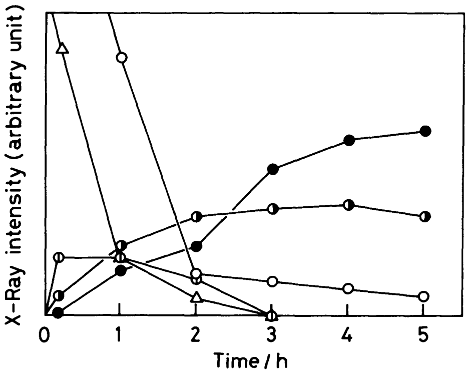

Fig. 2. X-Ray diffraction intensities of the products of $Si_3(PO_4)_4$-CaO reaction (1 : 3) at 940 °C.
○: $Si_3(PO_4)_4$ ($2\theta=11.0°$, 003), △: CaO ($2\theta=37.4°$, 200), ⦶: β-$Ca_3(PO_4)_2$ ($2\theta=31.0°$, 217), ◑: β-$Ca_2P_2O_7$ ($2\theta=29.6°$, 008), ●: α-cristobalite ($2\theta=21.9°$, 100).

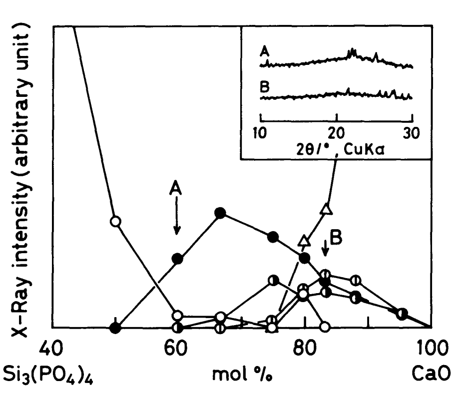

Fig. 3. Relation between CaO-content in the mixtures of $Si_3(PO_4)_4$-CaO and X-ray diffraction intensities of the products after heating at 940 °C for 5 h.
○: $Si_3(PO_4)_4$, △: CaO, ⦶: β-$Ca_3(PO_4)_2$, ◑: β-$Ca_2P_2O_7$, ●: α-cristobalite.

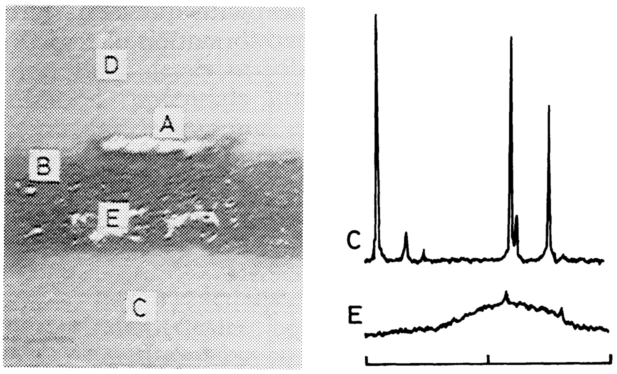

Fig. 4. Micrograph of cross section and X-ray diffraction patterns of the $Si_3(PO_4)_4$-CaO diffusion couple after heating at 940 °C for 72 h.
A: Pt marker, B: Interface before reaction, C: $Si_3(PO_4)_4$ phase, D: CaO phase, E: Product phase.

silicate compounds was observed because the acidity of P_2O_5 is higher than that of SiO_2.[6] The variation in the amounts of the crystalline product with the heating time at 940 °C is shown in Fig. 2. At the first step of the reaction, β-$Ca_3(PO_4)_2$ was formed predominantly. However, the amount of β-$Ca_3(PO_4)_2$ decreased and those of β-$Ca_2P_2O_7$ and α-cristobalite increased with the lapse of time. No changes in the fraction of each product were found after 4 h. Figure 3 shows the relation between the CaO content in the mixtures of the $Si_3(PO_4)_4$-CaO system and the X-ray diffraction intensities of the products, together with the X-ray diffraction patterns of typical products. It was found that the reaction products were also changed by the CaO content. In the region of a low CaO content, β-$Ca_2P_2O_7$ and α-cristobalite were mainly formed as crystalline products. Along with an increase in the CaO content, the fraction of β-$Ca_3(PO_4)_2$ increased and that of α-cristobalite decreased. It was also noticeable that the halation at $\theta=17$—25° became larger with a decrease in the CaO content.

Figure 4 shows a micrograph of a cross-section of the $Si_3(PO_4)_4$-CaO diffusion couple after the reaction. It can be seen that a semitransparent layer (*E*) about 0.5 mm thick was formed on the side of the $Si_3(PO_4)_4$ phase (*C*). This means that the reactions occurred by means of the one-way diffusion of CaO into the $Si_3(PO_4)_4$ phase. X-ray diffraction revealed that the surface of the $Si_3(PO_4)_4$ tablet was a mixture of trace amounts of β-$Ca_3(PO_4)_2$ and α-cristobalite, along with a large amount of an X-ray amorphous product such as silicon phosphate glass.[6–8] The halation caused by the formation of glass was clearly observed.

$Si_3(PO_4)_4$-MgO System. The reaction behavior of the $Si_3(PO_4)_4$-MgO system was found to be similar to that of the $Si_3(PO_4)_4$-CaO system. In the $Si_3(PO_4)_4$-MgO system, $Mg_3(PO_4)_2$ was observed to be present at higher temperatures than was β-$Ca_3(PO_4)_2$ in the latter system, and the amount of α-cristobalite was lower than in the latter system. In the reaction of the $Si_3(PO_4)_4$-MgO diffusion couple, a semitransparent layer just like the layer (*E*) in Fig. 4 was also observed.

The reactions of silicon phosphates with CaO and MgO were also carried out using SiP_2O_7 (**2**) instead of $Si_3(PO_4)_4$; the results were quite similar to those described above.

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