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The Reactions of the $(ZrO)_2P_2O_7$-NiO System and the ZrP_2O_7-NiO System

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Synopsis. The reaction between $(ZrO)_2P_2O_7$ and NiO at elevated temperatures up to 1340 °C yielded $Ni_3(PO_4)_2$ and ZrO_2 over the whole composition. The reaction between ZrP_2O_7 and NiO yielded $NiO\cdot 4ZrO_2\cdot 3P_2O_5$ and $Ni_3(PO_4)_2$ in the molar ratios up to equimolarity.

The ternary ZrO_2–CaO–P_2O_5 system was investigated by Bremser,[1] who reported the formation of $CaZr(PO_4)_2$ in the reaction of ZrP_2O_7 with $CaCO_3$. Recently, Šljukič *et al.* obtained the compound $M^IM_2'^{IV}(PO_4)_3$ (M=alkali metal and M′=Zr, Ti, Th, and U) by reacting the quadrivalent metal oxide with the alkali metal phosphate in the presence of B_2O_3 flux and investigated these compounds crystallographically.[2] They found that only $NaTh_2(PO_4)_3$ among these compounds showed piezoelectricity.[3] More recently, Allulli *et al.* prepared $ZrM(PO_4)_2\cdot 4H_2O$ (M=Mn^{II}, Co^{II}, NiO^{II}, Cu^{II}, and Zn^{II}) by treating ionex-changeable $ZrHNa(PO_4)_2\cdot 5H_2O$ with bivalent metal ions and obtained anhydrous phosphates $MZr(PO_4)_2$ by heating the resultant phosphates at higher temperature. These phosphates showed X-ray diffraction patterns similar to those of $CaZr(PO_4)_2$.[4]

However, few studies have been reported concerning the reaction of $(ZrO)_2P_2O_7$ and ZrP_2O_7 with other metal oxides, so the investigation of these reactions will be of interest.

Experimental

Materials. ZrP_2O_7 was prepared by a method similar to that used by Amphlett *et al.*[5] Zirconium phosphate gel was precipitated by adding 1.0 mol dm^{-3} H_3PO_4 to 0.4 mol dm^{-3} $ZrO(NO_3)_2$ solution containing 0.1 mol dm^{-3} HNO_3, the molar ratio of PO_4/Zr being 2.5. The gel was calcined at 1050 °C for 5 h. $(ZrO)_2P_2O_7$ was obtained by calcining ZrP_2O_7 at about 1600 °C for 1 h in a propane-oxygen furnace.

The calcined powder of ZrP_2O_7 and $(ZrO)_2P_2O_7$ was separately pulverized to particles under 74 μm in diameter with an agate ball mill. The purity of these materials was 99.5 wt% or more.

NiO was prepared by calcining nickel hydroxide, which was obtained by mixing 0.5 mol dm^{-3} $Ni(NO_3)_2$ solution with an excess of 0.5 mol dm^{-3} NaOH solution. The nickel hydroxide was calcined at 300 and 600 °C for 3 h.

Reactions at the Contact Surface of One-paired Tablets. The specimen powder was pressed into a tablet of 20 mm in diameter by about 5 mm in thickness under a pressure of 500 kg cm^{-2}. The NiO-tablet was placed on a $(ZrO)_2P_2O_7$-tablet and was heated for 24 h at 1200 °C in a SiC-furnace. After these tablets were removed from the furnace, the reaction products in the surface layers of the tablets were scraped off and examined by X-ray powder diffractometry. ZrP_2O_7 and NiO tablets were similarly heated at 1000 °C for 24 h.

Reactions in the Mixtures of Various Concentrations. The mixture of $(ZrO)_2P_2O_7$ and NiO or that of ZrP_2O_7 and NiO was wet with acetone and thoughly mixed for 30 min in an agate mortar. Then the mixture was pressed under a pressure of 500 kg cm^{-2} to form tablets weighing 0.3 g (10 mm in diameter and about 1.5 mm in thickness). The molar fraction of NiO in both systems was varied from 0.1 up to 0.9 at intervals of 0.1. The tablets were heated at 1200 °C for 24 h. The reaction products in the samples were determined by X-ray diffraction analysis.

Equimolar powder mixtures of both systems were subjected to DTA (heating rate: 10 °C/min, in air).

Isolation and Chemical Analysis of the Reaction Product Insoluble in HCl. The equimolar mixture of ZrP_2O_7 and NiO was heated at 1100 °C for 24 h and for an additional hour at 1400 °C. After $Ni_3(PO_4)_2$ was dissolved by boiling with 6 mol dm^{-3} HCl for 1 h, ZrO_2 in the insoluble residue was removed by flotation with 0.04 mol dm^{-3} sodium lauryl sulfate solution. The final residue thus obtained could not be identified from the known data. The P_2O_5, ZrO_2, and NiO in this unknown product were gravimetrically determined as $Mg_2P_2O_7$,[6] ZrO_2,[7] and bis(dimethylglyoximato)nickel(II)[8] respectively.

Results

Products. In the products of all systems, $Ni_3(PO_4)_2$ and monoclinic ZrO_2 were found. Nickel orthophosphate agreed with the compound existing in the NiO–P_2O_5 binary phase diagram.[9] The chemical formula of the unknown product was $NiO\cdot 4ZrO_2\cdot$

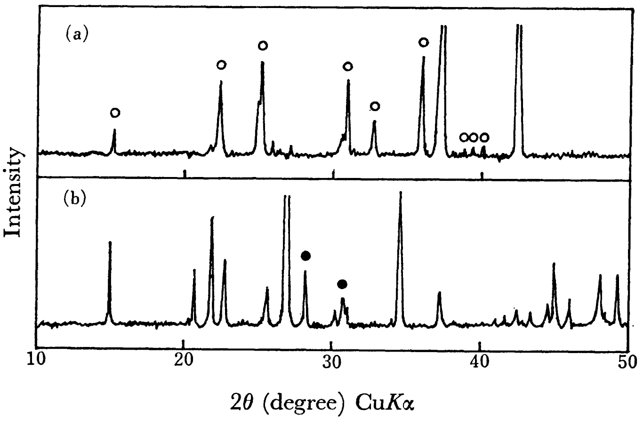

Fig. 1. X-Ray powder diffraction patterns of the surface layer of (a) NiO and (b) $(ZrO)_2P_2O_7$ tablet. (1200 °C). (a) ○: $Ni_3(PO_4)_2$, no mark: NiO, (b) ●: ZrO_2 (monoclinic), no mark: $(ZrO)_2P_2O_7$.

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$3P_2O_5$ or $NiZr_4(PO_4)_6$ (Found: NiO, 7.77; ZrO_2, 48.88; P_2O_5, 43.77 wt %. Calcd: NiO, 7.52; ZrO_2, 49.60; P_2O_5, 42.88 wt %). The color of this substance was purple-red. The X-ray powder diffraction pattern of this substance was quite different from that of $NaZr_2(PO_4)_3$ or $CaZr(PO_4)_2$.[10)]

Reactions at the Contact Surface of One-paired Tablets. *$(ZrO)_2P_2O_7$–NiO System*: X-Ray diffraction patterns of the surface layers of pair of NiO–$(ZrO)_2P_2O_7$ tablets are shown in Fig. 1. The $Ni_3(PO_4)_2$ was formed in the surface layer of the NiO-tablet and ZrO_2 in that of the ZrP_2O_7-tabelt. Hence, the reaction in each tabelt can be represented by the following equations:

$$(ZrO)_2P_2O_7 \longrightarrow 2ZrO_2 + P_2O_5, \quad (1)$$

$$3NiO + P_2O_5 \longrightarrow Ni_3(PO_4)_2. \quad (2)$$

This result is similar to that for the MgO–$Mg_2P_2O_7$ system reported by Jagisch and Bengtson, that is, $Mg_3(PO_4)_2$ was formed in the surface layer of the MgO-tablet by the cross diffusion of P_2O_5.[11)]

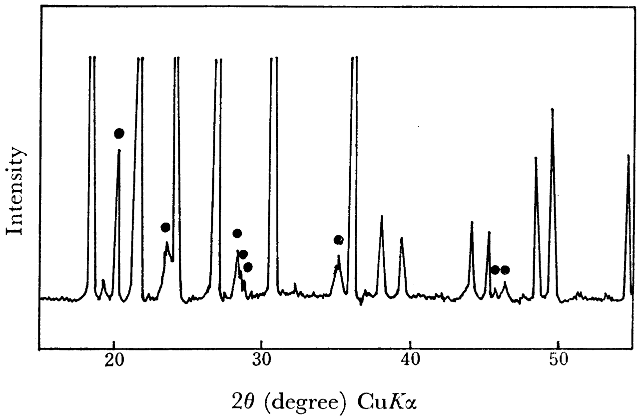

Fig. 2. X-ray diffraction pattern of the surface layer of ZrP_2O_7 tablet. (1000 °C).
●: $NiO\cdot4ZrO_2\cdot3P_2O_5$, no mark: ZrP_2O_7.

ZrP_2O_7–NiO System: X-Ray diffraction pattern of the surface layer of the ZrP_2O_7-tablet is shown in Fig. 2. In the surface layer of the NiO-tablet, $Ni_3(PO_4)_2$ was formed as shown in Fig. 1(a). The $NiO\cdot4ZrO_2\cdot3P_2O_5$ was formed in the surface layer of the ZrP_2O_7-tablet. Accordingly, this reaction proceeded *via* inter-diffusion. The reaction in each tablet can be represented by the following equations:

$$4ZrP_2O_7 + NiO \longrightarrow NiO\cdot4ZrO_2\cdot3P_2O_5 + P_2O_5, \quad (3)$$

$$3NiO + P_2O_5 \longrightarrow Ni_3(PO_4)_2. \quad (4)$$

Reactions in the Mixtures of Various Concentrations. In the $(ZrO)_2P_2O_7$–NiO system, $Ni_3(PO_4)_2$ and ZrO_2 were formed over the whole composition, although the maximum in the formation of these products were found at the NiO/$(ZrO)_2P_2O_7$ ratio of 3. In the ZrP_2O_7–NiO system, the formation of $NiO\cdot4ZrO_2\cdot3P_2O_5$ increased with the increasing molar ratio up to unity. When the ratio of NiO/ZrP_2O_7 exceeded one, $NiO\cdot4ZrO_2\cdot3P_2O_5$ was not formed, but $Ni_3(PO_4)_2$ and ZrO_2 were formed. In the reaction of the equimolar mixture, $NiO\cdot4ZrO_2\cdot3P_2O_5/Ni_3(PO_4)_2$ was nearly equal to unity. Accordingly, the reaction can be represented by the following equation:

$$4ZrP_2O_7 + 4NiO \longrightarrow NiO\cdot4ZrO_2\cdot3P_2O_5 + Ni_3(PO_4)_2 \quad (5)$$

DTA thermograms of both systems of the equimolar mixture showed a broad exothermic peak ranging between 800 and 1150 °C and a sharp endothermic peak at 1340 °C. The former was attributed to the formation of certain reaction products and the latter to the elutectic point[9)] of $Ni_3(PO_4)_2$ and NiO. A small endothermic peak at 300 °C in the ZrP_2O_7–NiO system was due to the structural conversion[12)] of ZrP_2O_7 from cubic to tetragonal.

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