Effect of ZrO\textsubscript{2} addition on water durability of FeO–Fe\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses

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We have studied the water durability of ZrO\textsubscript{2} containing FeO–Fe\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses for the immobilization of nuclear waste including Zr isotope. ZrP\textsubscript{2}O\textsubscript{7} crystals with 1–2 micrometer in diameter were precipitated in the glass matrix incorporated with \( \geq 1 \text{ mol}\% \) ZrO\textsubscript{2}. The molecular structure of phosphate network including ZrP\textsubscript{2}O\textsubscript{7} precipitates was analyzed by micro-Raman spectroscopy. Formations of Q\textsubscript{1} and Q\textsubscript{0} phosphate units contributing to better water durability are ascribed to preferential precipitation of ZrP\textsubscript{2}O\textsubscript{7} crystals with Q\textsubscript{1} units and the compensation of phosphate component in residual glass matrix.

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1. Introduction

Phosphate glasses generally have wide compositional range for glass formation with relatively low glass transition temperature as candidates for nuclear waste immobilization. In particular, binary iron phosphate glasses have been investigated to immobilize special nuclear wastes as a potential host due to distinguished chemical durability\textsuperscript{1} and loading capacity.\textsuperscript{3} For example, iron phosphate glasses are considered to be suitable for the host to solidify the radioactive sludge including sulfate.\textsuperscript{3} Since large amount of the sludge as secondary nuclear wastes containing BaSO\textsubscript{4} was unintentionally generated at the Fukushima Dai-ichi nuclear power plant, a proper material including glass should be developed to immobilize BaSO\textsubscript{4}.\textsuperscript{3}\textsuperscript{3} In a previous paper, BaSO\textsubscript{4} was contained in iron phosphate glasses as BaO (SO\textsubscript{3} < 0.1 mol\%) by a conventional melt quenching process.\textsuperscript{4} The BaO-containing iron phosphate glasses have relatively low process temperatures (1150–1200°C) and good water durability.\textsuperscript{4} The water durability for boiled water was evaluated by the weight loss per a specific surface area after immersion test at 120°C for 72 h.\textsuperscript{4} Some glasses with 10–20 mol\% BaO content possessed excellent water durability without macroscopic shape change after the immersion test and with small weight losses per a specific area less than \( 1.0 \times 10^{-9} \) kg/mm\textsuperscript{2}. The results were considered from glass network structure\textsuperscript{5,6} and surface microstructure.\textsuperscript{6} Our previous studies\textsuperscript{5,6} revealed that the addition of BaO originated from the main component of the sludge had resulted in the improvement of water durability for FeO–Fe\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses.

The high-level radioactive wastes (HLWs), which are stored in Rokkasho-village, have been solidified by use of borosilicate glasses. However, new, alternative glass hosts are sought for storing of precipitated zirconium molybdate [Zr(OH)\textsubscript{2}·Mo\textsubscript{2}O\textsubscript{7}·(H\textsubscript{2}O)\textsubscript{2}] sludge.\textsuperscript{7} The high loading capacity is one of the critical properties to minimize the total volume of glass wasteforms. The iron phosphate-based glasses are ones of potential hosts for the zirconium molybdate sludge in terms of large loading capacity in MoO\textsubscript{3}.\textsuperscript{8} Since Zr isotope in HLWs mainly originates from fuel cladding materials, e.g., zircaloy etc.,\textsuperscript{9} less solubility of ZrO\textsubscript{2} remains to be solved so as to be chosen the host glass among various phosphate glasses. Wang et al. reported that ZrP\textsubscript{2}O\textsubscript{7} crystalline phase precipitated in Na\textsubscript{2}O–Fe\textsubscript{2}O–Fe\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses containing > 6 mol\% ZrO\textsubscript{2}.\textsuperscript{10} However, the chemical durability of the iron phosphate glasses related to precipitated ZrP\textsubscript{2}O\textsubscript{7} crystalline phase has not been reported to date.

In this paper, we report the water durability of FeO–Fe\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses including ZrP\textsubscript{2}O\textsubscript{7} precipitates. A compositional trend of phosphate network by incorporation of ZrO\textsubscript{2} was obtained using micro-Raman spectroscopic technique. The relationship between the corrosion characteristic and phosphate structure is also discussed.

2. Experimental procedure

The nominal molar compositions expressed as \( x\text{ZrO}_2–(100–x)(0.3\text{FeO}_2–0.7\text{P}_2\text{O}_5) \) with \( x = 0, 1, 2, 3, 5, \) and 10 and \( y = 1–1.5 \) were studied. The samples were prepared
by a conventional melt quenching technique. Raw materials were ZrO$_2$ reagent and 0.3FeO$_y$-0.7P$_2$O$_5$ glass powder prepared in advance. The raw materials with 25 g totally were weighed and were subsequently mixed using alumina mortar and pestle. The batch was placed in a platinum crucible and was melted in air at 1300°C for 1 h. The melt was quenched onto a carbon plate, immediately annealed at the glass transition temperature for 1 h and then cooled to room temperature with a rate of $\approx$1°C/min. The quenched samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analyses.

Bulk glass samples had been fractured into a large number of pieces with difficulty for weighing after immersion test due to MCC-2 static leaching method in preliminary experiments. The immersion test was then conducted by product consistency test method B (PCT-B) for powdered samples. The pulverized sample with 75–150 μm in diameter was immersed in ultrapure water with a resistivity of 18.2 MΩ·m and with 50 mL in volume for the PCT-B. Then powdered sample in a polytetrafluoroethylene sealed vessel (TAF-SR-50, Taiatsu Techno. Co., Japan) was held at 90°C for 168 h. The water durability of the samples was evaluated by normalized release rate ($NR_i$). The Fe and P contents of the solution were determined by inductively-coupled plasma mass spectroscopy (ICP-MS, VARIAN820-MS, Australia). Solutions for ICP-MS were diluted to 5–100 ppt using 3% HNO$_3$ aqueous solution. The $NR_i$ was estimated using the Eq. (1).

$$NR_i = \frac{C_i}{f_i \cdot \left(\frac{SA}{V}\right) \cdot t}$$  \hspace{1cm} (1),

where $NR_i$ [g/(cm$^2$·day)] is the normalized release rate for $i$-th element, $C_i$ (g) is the water diluted weight for $i$-th element, $f_i$ is the fraction of $i$-th element in glass, $SA/V$ is the surface area of the glass form divided by the leachate volume, and $t$ is the immersion time (day). The relative surface area of samples was estimated by BET method (FlowSorb II 2300, SHIMADZU, Japan). The values of $NR_i$ were averaged using the samples at least two times.

Micro-Raman spectra were collected from each polished glass and synthesized ZrP$_2$O$_7$ crystalline sample using a Raman spectrometer (NRS-5100, JASCO, Japan) with a 532 nm YAG laser as an excitation light source. The output power of the laser was $\approx$50 mW with a focused beam on an area with $\approx$10 μm in diameter using a 50× objective lens. At least two spots on the glass were inspected to check the reproducibility of the spectrum.

### 3. Results and discussion

Figure 1 shows XRD patterns of as-prepared $x$ZrO$_2$–(100 – $x$)(0.3FeO$_y$-0.7P$_2$O$_5$) samples for $x$ = 0–10 mol % with a step of ZrO$_2$ substitution. ZrP$_2$O$_7$ phase is detected in the samples with $x$ ≥ 3. Figure 2 shows a SEM image with EDS elemental mappings of the 10 mol %ZrO$_2$ glass as a typical example. Both Zr and P elements were detected for the precipitates supporting ZrP$_2$O$_7$ phase. The microstructure observation by SEM-EDS revealed that the

![Fig. 1. XRD patterns of samples with a composition of $x$ZrO$_2$–(100 – $x$)(0.3FeO$_y$-0.7P$_2$O$_5$) for $x$ = 0–10 mol %.

![Fig. 2. SEM-EDS analysis for the $x$ = 10 sample. (a) SEM image, (b) Fe, (c) P, and (d) Zr elemental mappings.](949)
spherical precipitates with diameters of 1–2 μm were distributed in the glass matrix. The precipitates also appeared in x = 1 sample with the X-ray halo pattern shown in Fig. 1. Distribution of the precipitates was increased monotonically with increasing ZrO₂ concentration for x = 1–10 mol% samples. The cation ratio of Fe/P analyzed for specific area of glass matrix by SEM-EDS was 0.39 ± 0.01 for x = 0 and 0.45 ± 0.07 for x = 10, respectively. It was seen that the larger ZrO₂ incorporation accompanied with larger Fe/P ratio in residual glass matrices.

**Figure 3** shows two linear trends of leaching rates of P and Fe elements for x = 0–10 mol% samples evaluated by the PCT-B method. The release rates were normalized with their initial concentrations. The leaching rate of P element decreases with increasing ZrO₂ concentration. The decreasing of the rate 3.5 × 10⁻⁷ g/(cm²·day) for P element was obtained for x = 10 sample. On the contrary, the leaching rate for Fe element has no change within experimental error in all samples. No Zr element was detected by ICP-MS measurements probably due to the superior water durability of ZrP₂O₇ precipitates.

**Figure 4** shows compositional dependence of Raman spectra for x = 0–10 samples. Raman spectrum of crystalline ZrP₂O₇ phase is also presented for comparison. Raman scattering bands were assigned to the phosphate Q₀ structures by the literature. The notation Qⁿ represents the number n of bridging oxygen per PO₄ tetrahedron. The bands at 1300 and 1200 cm⁻¹ correspond to respective asymmetric and symmetric stretching modes with non-bridging oxygen for PO₄ Q² units. The bands at 1130 and 1060 cm⁻¹ are due to P–O asymmetric and symmetric stretching modes with non-bridging oxygen for Q¹ units. The band at 1005 cm⁻¹ is attributed to the symmetric P–O stretching mode of non-bridging oxygen in orthophosphate Q⁰ units. The asymmetric P–O–P stretching mode of Q⁰ units produces a peak at 930 cm⁻¹. The bands at 750 and 710 cm⁻¹ are due to the symmetric P–O–P stretching mode with non-bridging oxygen in Q¹ units and the P–O–P stretching mode with bridging oxygen in Q² units, respectively. The intensity of the peak at 1200 cm⁻¹ for phosphate Q² units decreases and relative-intensities of the bands at 1130 and 1060 cm⁻¹ for Q¹ units increase with increasing ZrO₂ concentration. The intensity of the main peak at 1090 cm⁻¹ for crystalline ZrP₂O₇ precipitate also increases with increasing ZrO₂ concentration due to the larger fraction of ZrP₂O₇ precipitates embedded in the glass matrix (Fig. 2).

The ZrP₂O₇ phase in the ZrO₂-containing glass samples has been detected by XRD analysis (Fig. 1). The SEM-EDS results also revealed that crystalline ZrP₂O₇ precipitates with 1–2 μm in diameter were formed and distributed in x ≥ 1 samples. Precipitated ZrP₂O₇ phase consists of (P₂O₇)₄ dimer units (Q¹). The formation of ZrP₂O₇ precipitates due to ZrO₂ incorporation results in the decrease of P₂O₅ concentration in the residual glass matrix with the variation of main phosphate structure from Q² to Q¹ and Q⁰ units.

The better water durability evaluated by the PCT-B method can be accounted for the reduction of the fraction of Q² chain units in the glass matrix, according to the compositional dependence of the Raman spectra. The macroscopic fractures observed for bulk ZrO₂ containing samples in the preliminary experiments, as described in the section 2, were probably attributed to the heterogeneity of microscopic structure due to ZrP₂O₇ precipitates with Q¹ units and the residual glass matrix with Q⁰ units and with remaining small amounts of Q² units contributing to poor water durability.

### 4. Conclusions

The present results describe the compositional dependences of water durability of FeO–Fe₂O₃–P₂O₅ glasses containing ZrO₂ for the purpose of immobilization of nuclear...
waste with Zr isotope. The variations of water durability and phosphate structure with ZrO$_2$ concentration were investigated. The crystalline ZrP$_2$O$_7$ precipitates appeared in the samples at $\geq 1$ mol% ZrO$_2$. Raman spectroscopy gives the insight that incorporation of ZrO$_2$ into the glass leads to the formation of ZrP$_2$O$_7$ phase with Q$^1$ units and those of PO$_4$ Q$^1$ and Q$^0$ units with small amounts of Q$^2$ units for residual glass matrices. The phosphate network variation from Q$^2$ to Q$^1$ and Q$^0$ units for the glass matrix with residual Q$^2$ species and the distribution of the ZrP$_2$O$_7$ precipitates contribute to microscopic heterogeneity and results in better water durability for weight loss by the PCT-B method and macroscopic fracture after the preliminary immersion tests for bulk samples.

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