Effect of molybdenum oxide addition on the durability and structure of iron phosphate glasses

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Molybdenum oxide (MoO3)-containing iron phosphate (Fe–P) glasses with an analyzed Fe/P molar ratio of 0.41–0.43 and 0–43 mol % MoO3 were prepared via a conventional melt-quenching method. The X-ray diffraction analysis revealed that all prepared samples had an X-ray non-crystalline state with a halo pattern. The dependency of the MoO3 concentration on the glass transition temperature and water durability were evaluated. The water durability was examined in terms of glass plates with dimensions of 10 × 10 × 3 mm3 via a static leaching test at 120 °C for 72 h using ultrapure water. Raman spectroscopy was used for the analysis of the PO4 5- structural units as well as both Mo5+ and Mo6+ species. The Fe–P glasses containing 8–17 mol % MoO3 consisted mainly of PO4 Q1 structural units as well as both Mo5+O6 distorted octahedra and Mo6+O6 octahedra and a Fe-related polyhedra with a minimization of P–O–P and Mo–O–Mo bonds. These structural features were qualitatively related to the improved properties of both thermal stability against crystallization and water durability for the MoO3-containing Fe–P glasses.

Key-words : Iron phosphate glass, Molybdenum, Durability, Structure, Raman spectroscopy

1. Introduction

Molybdenum (Mo) is one of the main elements of the insoluble residues occurring in high-level concentrated liquids and condensate storage tanks. Mo oxide (MoO3) has low solubility in the ordinal borosilicate glasses prepared using the glass vitrification method.1,2) Meanwhile, iron phosphate (Fe–P) glasses have good glass formation ability when containing a large amount of MoO3.3–8) Numerous reports on glass formation have been compiled, including those in terms of basic properties such as density and characteristic temperature as well as the structures of MoO3–Fe2O3–P2O5,9) and the Mo5+/Mo6+ species. The Fe–P glasses containing 8–17 mol % MoO3 consisted mainly of PO4 Q1 structural units as well as both Mo5+O6 distorted octahedra and Mo6+O6 octahedra and a Fe-related polyhedra with a minimization of P–O–P and Mo–O–Mo bonds. These structural features were qualitatively related to the improved properties of both thermal stability against crystallization and water durability for the MoO3-containing Fe–P glasses.

2. Experimental procedure

2.1 Glass sample

To add MoO3 as a simulated waste component to the greatest extent possible, we selected a glass batch composition of 30 mol % Fe2O3 and 70 mol % P2O5 (46.2 mol % FeO–53.8 mol % P2O5), which had a moderate durability for handling in an ambient atmosphere. The mixed batch for the Fe–P glass was melted at 1,300 °C for 1 h in air using a platinum (Pt) crucible and then quenched prior to the addition of MoO3. The Fe–P glass cullet ground to less than 300 μm in size and commercial MoO3 powder (>99.5 % purity, Kanto Chemical Co., Inc., Tokyo, Japan) were thoroughly mixed using an alumina mortar and pestle for the batch compositions of xMoO3–(100 − x)(0.46FeO–0.54P2O5), x = 10–50 mol %. Following this, 20 g of the mixed batch was melted using a Pt crucible, depending on glass composition, at 930–1,150 °C for 1 h in air. The melt was then poured into a graphite mold and subsequently annealed at around the glass transition temperature.
perature before being gradually cooled to room temperature at a rate of 1 °C/min.

The valence state of the Mo and Fe in Mo–Fe–P glasses can be presented as Mo$_{5+}$/Mo$_{6+}$ and Fe$_{2+}$/Fe$_{3+}$, respectively. Bai et al. noted that the separate valence state of Mo and Fe ions could not be determined using the titration technique. Thus, after melting the concentrations of the cationic elements Mo, Fe, and P were evaluated via scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis. Three to five measurements were made for composition analysis, and the averaged value with error range was determined for each composition.

Table 1 summarizes the glass batch and analyzed compositions with a characterization of the molar ratios of Mo/(Mo + Fe), Mo/P, and Mo/P, whereas Fig. 1 shows each of the analyzed glass compositions examined in the MoO$_3$–FeO$_x$–P$_2$O$_5$ system. Table 1 also indicates the melting temperature for each glass sample.

### 2.2 Evaluation

In terms of the quenched samples, the existence of crystalline and non-crystalline phases was evaluated using a powdered X-ray diffraction (XRD) technique (X’Pert Powder Diffractometer, PANalytical, Netherlands) in the 2θ range of 10–90°. The characteristic temperatures of the glass transition, $T_g$, and the onset of crystallization, $T_c$, were determined via thermogravimetry–differential thermal analysis (TG–DTA) (Thermo plus Evo TG–DTA, Rigaku, Tokyo, Japan). The TG–DTA curve was measured at a heating rate of 10 °C/min in the temperature range of room temperature to 900 °C.

Meanwhile, the water durability was evaluated via immersion tests at 120 °C/min for 72 h on the basis of the MCC-2 leaching test method using the 10 × 10 × 3 mm$^3$ glass plate with six polished surfaces in ultrapure water with 50 mL in volume at 18.2 MΩ·cm. The sample was suspended by a fluoroethylene resin thread in a PTFE sealed vessel (TAF-SR-50, Taiatsu Techno Co., Tokyo, Japan) following the immersion tests, we evaluated the weight loss per specific area, $\Delta W/S$, where $\Delta W$ is the weight change and $S$ is the surface area.

The Raman scattering spectra were measured using a laser Raman spectrometer (inVia™, RENISHAW, United Kingdom) in the range of 400–1,400 cm$^{-1}$ to characterize the PO$_4$ Q$^n$ structure and molybdate species, where $n$ is the number of bridging oxygens per PO$_4$ tetrahedron.

### 3. Results

#### 3.1 XRD analysis

Figure 2 shows the XRD patterns of all the prepared Fe–P samples with 0–43 mol% MoO$_3$. The results confirmed that all samples had an X-ray non-crystalline state with a halo pattern.

#### 3.2 Glass transition temperature

Figure 3 shows representative DTA curves of the Fe–P and MoO$_3$-containing Fe–P glasses. At only 0 mol% MoO$_3$, we observed both a glass transition temperature of...
Tg and the onset of crystallization, Tx, then the exothermic peak of the crystallization, and, finally, the endothermic peak due to melting at ³850 °C. Using TG–DTA runs based on those used in previous studies,6),7) we found that all the MoO3-containing Fe–P glasses exhibited a Tg with endothermic behavior and had no Tx without crystallization behavior in the range of room temperature to 900 °C. One of our previous studies,15) in which we used a commercial DTA apparatus, demonstrated that the case without crystallization behavior (no Tx) indicated excellent thermal stability against crystallization, while in the case with Tx, the difference between Tx and Tg was used for a parameter expressing relative thermal stability.

Figure 4 shows the variation in Tg depending on the MoO3 concentration in Fe–P glasses with/without MoO3. The Tg results indicated that at 8–17 mol % MoO3, the Tg values were scattered between 500 and 530 °C independent of MoO3 concentration and that a plateau region existed. The Tg also decreased gradually with an increase in MoO3 concentration at 17–43 mol % MoO3.

3.3 Water durability

Figure 5 shows the variation in the weight loss per specific area (ΔW/S) in relation to the MoO3 concentration in the glass plate samples, as well as the representative macroscopic appearances following the immersion tests. The ΔW/S decreased with a MoO3 concentration of between 0 and 26 mol % before it increased again at a concentration of ≥39 mol %. At 43 mol % MoO3, the glass samples fully dissolved into the ultrapure water following the immersion test, and the ΔW/S could not be determined. At 8–26 mol % MoO3, the evaluation using the ΔW/S revealed that the MoO3-containing Fe–P glasses were superior in terms of water durability (Fig. 5).

3.4 Glass structure

Figure 6 shows the Raman scattering spectra of the FeO–Fe2O3–P2O5 and MoO3–FeO–Fe2O3–P2O5 glasses. The Raman scattering bands observed were assigned according to the results of previous studies.6)–10),12) In the 46.3 mol %FeO–53.7 mol %P2O5 glass without MoO3, the Raman scattering bands at ~1,200 and ~1,080 cm⁻¹ were observed because of the symmetric Q2 and Q1 stretching modes of the PO4 tetrahedra, respectively. With the increase in MoO3 concentration, the symmetric vibration modes of the PO4 Qn structure observed mainly in the Raman spectra varied from Q2 to Q1 and to Q0 (at ~940 cm⁻¹).

The molybdate constituent formed MoO6 octahedral units. In the composition range of 8–17 mol % MoO3, with, for the most part, no change in Tg (Fig. 4), the symmetric stretching mode of Mo5+O6 distorted octahedra (or five
in MoO$_3$ concentration, the P$_2$O$_3$ concentration decreased and the morphology of the PO$_4$ tetrahedra varied from Q$^2$ to Q$^1$ units. (2) With regard to the molybdate structural unit, at 8–17 mol % MoO$_3$, both Mo$^{5+}$O$_6$ distorted octahedra and Mo$^{6+}$O$_6$ octahedra formed. Bai et al.$^7$ also confirmed the existence of Mo$^{5+}$O$_6$ distorted octahedra in a similar glass composition. At 26–43 mol % MoO$_3$, Mo$^{6+}$O$_6$ octahedra were mainly present. (3) At 39–43 mol % MoO$_3$, where the ratio of MoO$_3$ to P$_2$O$_5$ was relatively high in our glass compositions, considerable Mo–O–Mo bonds were observed.

As shown in Fig. 3, no crystallization behavior was observed in the DTA curves of the Fe–P glasses containing MoO$_3$. That is, the addition of MoO$_3$ enhanced the thermal stability against crystallization of the Fe–P glasses at high temperatures of 500–900 °C in the DTA curves. Given the relationship between the thermal stability and the glass structure, the MoO$_3$ constituent played the role of a reticulator,$^{17}$ connecting the phosphate networks, while the formation of Mo–O–P and Mo–O–Mo bonds contributed to the enhancement of the thermal stability. Similarly, Tricot and Vezin$^{18}$ revealed via magnetic resonance spectroscopy that P–O–V$^{5+}$ bonds were formed in sodium vanado–phosphate glasses and that the V$^{5+}$O$_6$ octahedral unit reticulated the phosphate network and contributed to the increase in glass transition temperature. Our $T_g$ results indicated there was almost no change in $T_g$ (500–530 °C) independently of MoO$_3$ concentration at 8–17 mol % MoO$_3$ (Fig. 4). In this composition range, the Raman spectra results suggested that the Mo$^{5+}$O$_6$ distorted octahedra$^{16}$ served as a reticulator to stabilize the phosphate network.

In the similar composition region of 8–26 mol % MoO$_3$, following the immersion test, the $\Delta W/S$ exhibited minimum values and resulted in good water durability for the MoO$_3$-containing Fe–P glasses (Fig. 5). The combination of the Raman spectroscopy (Figs. 6 and 7), $^{57}$Fe Mössbauer spectroscopy,$^{20}$ and neutron magnetic diffraction results$^{21}$ led to the conclusions regarding the formation of both Mo$^{5+}$O$_6$ distorted octahedra and Mo$^{6+}$O$_6$ octahedra,$^{6,17,16,19}$ Fe$^{3+}$O$_6$ octahedral and Fe$^{3+}$O$_4$ tetrahedral units,$^{20,21}$ Q$^1$-based phosphate networks with Mo–O–P bonds, and the minimization of the Mo–O–Mo bonds. Similarly, it has been observed that in Fe–P glasses, the substitution of Fe–O–P bonds for P–O–P bonds due to Fe$_2$O$_3$ addition contributes to the improvement in water durability.$^{3,4}$

Figure 8 shows the proposed schematic structure of Fe–P glasses containing 8–17 mol % MoO$_3$ with good thermal stability and water durability. The Raman spectroscopy results (Figs. 6 and 7) indicated that the MoO$_3$-containing Fe–P glasses consisted mainly of Q$^1$ PO$_4$ tetrahedral units with P–O–Fe bonds and contained Q$^0$ and Q$^2$ units as minority species. It has been suggested that for molybdate units, Mo$^{5+}$O$_6$ distorted octahedra (Mo$^{5+}$O$_6$ square pyramids) and Mo$^{6+}$O$_6$ octahedra co-exist and connect with PO$_4$ units to form a three-dimensional network, which is somewhat similar to the MoOPPO$_4$ (Mo$_2$O$_2$:P$_2$O$_5$) crystal.

**Figure 6.** Raman spectra of the Fe–P and MoO$_3$-containing Fe–P glasses.

**Figure 7.** Variation of relative intensity ratios of the specific Raman scattering bands in the Fe–P and MoO$_3$-containing Fe–P glasses.

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**Figure 7.** shows the features of the Raman scattering bands in the MoO$_3$-containing Fe–P glasses. The relative intensity ratios of a number of the Raman scattering bands led to an understanding of the variation in network structure and chemical bonding in relation to the MoO$_3$ concentration. The following three features were observed. (1) The relative intensity ratio of the symmetric vibrational modes of the PO$_4$ Q$^1$ and Q$^2$ units increased with the addition of MoO$_3$, which indicated that, with an increase
The $^{57}$Fe Mössbauer spectroscopy and high-performance liquid chromatography results demonstrated that the iron oxide species appeared mainly as Fe$^{3+}$O$_4$ tetrahedra and Fe$^{2+}$O$_6$ octahedra, while they also appeared as Fe$^{2+}$O$_3$. Previous research involving the $^{57}$Fe Mössbauer spectroscopy, neutron diffraction, and neutron magnetic diffraction revealed that Fe–P glasses contain a FePO$_4$-like structure that includes Fe$^{3+}$O$_4$ tetrahedra and a (Fe$_2$O$_3$)$_3$ cluster consisting of both a Fe$^{2+}$O$_6$ trigonal prism and two Fe$^{3+}$O$_6$ octahedra.

With regard to the valence state of Mo, in the MoO$_3$–FeO–Fe$_2$O$_3$–P$_2$O$_5$ glasses, Mo$^{5+}$ species existed with a relatively large fraction of Mo$^{5+}$/Mo$_{total}$ = 40%, whereas the BaO–ZnO–MoO$_3$–P$_2$O$_5$ glasses contained a small fraction of Mo$^{5+}$ species (Mo$^{5+}$/Mo$_{total}$ = <5%). The evidence of the iron oxide constituent related to the existence of Mo$^{5+}$ suggested that the Mo$^{5+}$ distorted octahedra were located near the Fe$^{3+}$O$_4$ and/or Fe$^{3+}$O$_6$ species. However, the existence/non-existence of Mo–O–Fe bonds was not determined in this study.

As described previously, superior characteristics of both thermal stability and water durability resulted from the complex network structures consisting of Mo$^{5+}$O$_6$ distorted octahedra and Mo$^{6+}$O$_6$ octahedra, PO$_4$ Q$^1$ units, Fe$^{3+}$O$_6$, Fe$^{2+}$O$_4$, and Fe$^{2+}$O$_6$ species, as did the minimization of the P–O–P and Mo–O–Mo bonds between the connecting PO$_4$ and Mo$^{6+}$O$_6$ units, respectively. This glass structure characteristic was achieved experimentally using the composition conditions of 8–17 mol % MoO$_3$, a Mo/P molar ratio of 0.08–0.19, and a Fe/P ratio of 0.42–0.43, as shown in Table 1. However, further studies are required for the quantitative analysis of the optimized structure of MoO$_3$-containing Fe–P glasses.

5. Conclusions

Fe–P glasses containing MoO$_3$ were prepared via a conventional melt quenching method and were subsequently evaluated in terms of characteristic temperature via DTA, water durability via static immersion tests, and glass structure via Raman spectroscopy. The plateau composition region with a constant glass transition temperature existed at 8–17 mol % MoO$_3$. In addition, MoO$_3$ independent glass composition. A similar composition range of 8–26 mol % MoO$_3$ had superior water durability according to the weight loss per specific area evaluation following the immersion tests. A combination of the Raman spectroscopy results and the findings of previous research revealed the appropriate glass structure for good thermal stability and water durability in Fe–P glasses containing MoO$_3$. The durable Mo–Fe–P glasses were composed mainly of PO$_4$ Q$^1$ units and Q$^3$ and Q$^2$ units as minority species as well as Mo$^{5+}$O$_6$ distorted octahedra and Mo$^{6+}$O$_6$ octahedra, whereas Fe$^{3+}$O$_4$, Fe$^{2+}$O$_6$, and Fe$^{2+}$O$_6$ species also appeared with the minimization of the P–O–P and Mo–O–Mo bonds between the connecting PO$_4$ and Mo$^{6+}$O$_6$ units, respectively.

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