Effect of ZnO content on crystallization tendency of Mo-bearing borosilicate glass

Jae-Young Pyo [a,*], Jong Heo [a], and Wooyong Um [a]
[a]*Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro. Nam-Gu. Pohang. Gyeongbuk, 37673, Republic of Korea*
[*]*Corresponding author: vywodud@postech.ac.kr*

1. Introduction

Vitrification is a method of immobilizing radionuclides in a glass matrix. Glasses are promising candidates for immobilization of high-level radioactive waste (HLW) from the reprocessing of spent nuclear fuels because they are chemically durable waste forms [1]. Borosilicate glasses are being developed to solidify radioactive waste in several countries such as the United States, United Kingdom, France, and Japan. Borosilicate glasses are considered suitable materials for eventual disposal as they allow for high waste loadings and are chemically durable. However, some HLW components have limited solubility in borosilicate glass melts [2]. Typically, cations with a high oxidation state such as Mo^{6+}, S^{6+}, P^{5+}, and Tc^{7+} are easily phase-separated in the borosilicate glass melt [3]. Molybdenum (Mo) is an abundant fission product in spent nuclear fuel and has low solubility (~ 1 mol% MoO_3) in the borosilicate glasses. Alkali or alkaline earth molybdate crystals are formed when Mo ions in excess of their solubility are added to borosilicate glasses. The alkali molybdate crystals are water-soluble and may contain the radionuclide ^{137}Cs (as in $CsLiMoO_4$), which deteriorates the chemical durability of the glasses [4]. Therefore, new glass formulations should be developed to improve the solubility of MoO_3 in borosilicate glass. This study investigated the influence of ZnO content on the crystallization tendency of borosilicate glasses containing MoO_3.

2. Methods

The baseline glass composition was 56 SiO_2 − 16 B_2O_3 − 4 Al_2O_3 − 18 Na_2O − 6 CaO (mol%), and different amounts of MoO_3 and ZnO were added depending on the sample type. The baseline composition was simplified from the SON68 glass composition [5]. The compositions of glass samples were shown in Table I. Mo2ZnX (X represents the ZnO contents in mol%) series glasses contained 2 mol% of MoO_3 and 0, 5, 10, and 15 mol% of ZnO were added. High purity powders of SiO_2, H_3BO_3, Al_2O_3, Na_2CO_3, $CaCO_3$, MoO_3, and ZnO were used as glass precursors. The batches of mixed powders were placed in alumina crucibles and melted in an electrical furnace under an ambient atmosphere at 1,250 °C for 2 h, and then cast on a brass mold. The obtained glasses were ground for homogenization and melted again in Pt/Au (95%Pt/5%Au) dishes. To simulate the natural cooling of radioactive waste glass in a canister, the melts were kept at 1,250 °C for 2 h, and then slowly cooled at a rate of 1 °C/min to room temperature.

Table I: Nominal compositions of the prepared glasses (in mol%)

	Mo2 Zn0	Mo2 Zn5	Mo2 Zn10	Mo2 Zn15
SiO_2	54.88	52.08	49.28	46.48
B_2O_3	15.68	14.88	14.08	13.28
Al_2O_3	3.92	3.72	3.52	3.32
Na_2O	17.64	16.74	15.84	14.94
CaO	5.88	5.58	5.28	4.98
ZnO	0	5	10	15
MoO_3	2	2	2	2
Nd_2O_3	0	0	0	0

All glass samples were analyzed by X-ray diffraction (XRD). For this analysis, glass samples were crushed into the fine powders. The morphology of the cross-section of the glasses was analyzed using a scanning electron microscope (SEM). The Zn and Mo K-edges X-ray absorption spectroscopy (XAS) data were obtained in the transmission mode on the 10C beamline of the Pohang Light Source (PLS). The XAS data were recorded for powdered reference materials and glass specimens attached to polyimide film. The extended X-ray absorption fine structure (EXAFS) spectra were converted to k ($Å^{-1}$) and weighted by k^2 to amplify at high k values. Then they were Fourier-transformed and fitted in the real space within interatomic distance $1 \leq R \leq 2$ Å using a 0.5 $Å^{-1}$ Hanning window. The average bond distances (R), Debye-Waller factor (σ^2), and the coordination numbers (CN) were determined through fitting procedures using the software ATHENA and ARTEMIS.

3. Results and discussion

3.1 XRD analysis

The XRD results of the Mo2ZnX series glasses, cooled at 1 °C/min, are shown in Fig. 1. Crystals of Na_2MoO_4 and $CaMoO_4$ were simultaneously observed in Mo2Zn0 glass. Also, the observed peaks of $Na_2MoO_4 \cdot 2H_2O$ were found because Na_2MoO_4 was partially hydrated by water vapor during the analysis process. The addition of 5 mol% of ZnO had a good effect in sufficiently inhibiting the formation of alkali

molybdate crystals, which deteriorated the chemical durability of radioactive waste glass. As the amount of ZnO was increased to 10 mol%, the intensity of peaks of $CaMoO_4$ decreased, and the glass with 15 mol% of ZnO was completely amorphous.

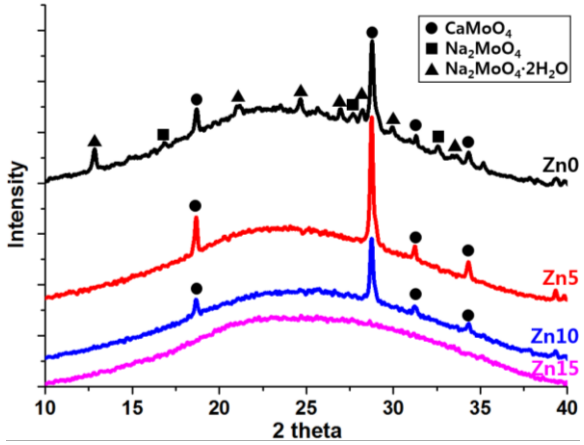

Fig. 1. XRD patterns of Mo2ZnX series glasses slowly cooled at 1 °C/min.

3.2 SEM analysis

Fig. 2 shows the SEM analysis of the cross-section of Mo2ZnX series glasses, and it was observed that the size of molybdate crystals decreased as ZnO was added to the borosilicate glasses. There were spherical molybdate crystals with a size of about 2.5 μm inside the Mo2Zn0 glass. Mo2Zn5 glass had molybdate crystals of size 2 μm, and the inside of Mo2Zn15 glass was homogeneous without any crystals. The SEM results, which were consistent with the XRD results, also showed that the size of molybdate crystals decreased as ZnO was added to the borosilicate glasses.

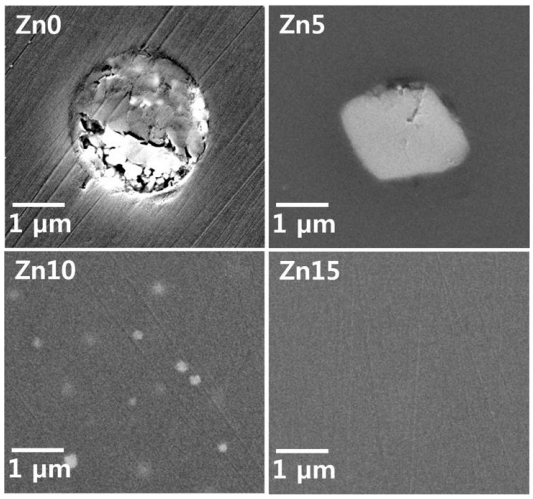

Fig. 2. SEM images of the cross-section of Mo2ZnX series glasses slowly cooled at 1 °C/min.

3.3 XAS analysis

The radial distribution function (RDF) curves obtained from Zn K-edge EXAFS spectra of ZnO and Mo2Zn10 were fitted and the results were shown in Fig. 3. ZnO was used as the reference for the fitting analysis to investigate the structure of Zn ions in the borosilicate glasses. The dominant contributions to the theoretical X-ray absorption spectrum of ZnO were the single scattering path with Zn–O at 1.965 Å (N=4) and Zn–Zn at 3.208 Å (N=12). These back-scattering paths were used to fit the first and second peaks in the RDF of ZnO by changing E_0, S_0^2, and σ^2 for each path with fixed values of R and N, respectively. By fitting ZnO, it was determined that S_0^2 = 0.72 and E_0 = 4.30 eV, which were also used as the fixed values during fitting process of the glass samples. EXAFS data showed that Zn ions were surrounded by 4.16 oxygen atoms at a distance of 1.94 Å.

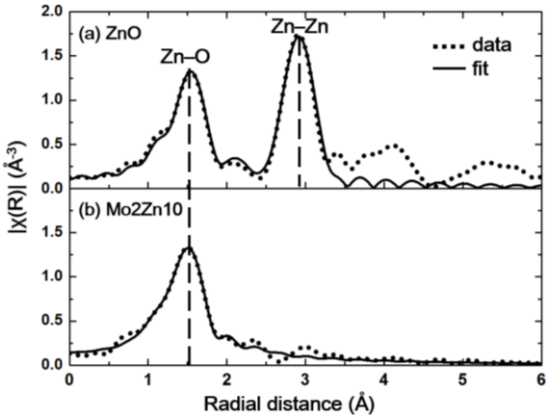

Fig. 3. The Fourier-transformed EXAFS from (a) ZnO and (b) Mo2Zn10 as a function of the distance from a Zn atom. The dotted lines show the experimental data and the solid lines are the fits.

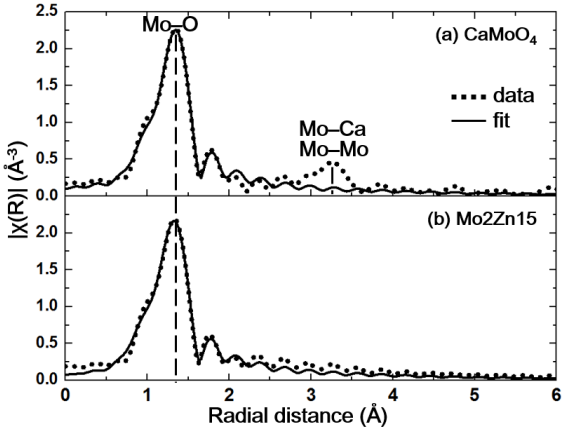

Fig. 4. The Fourier-transformed EXAFS from (a) $CaMoO_4$ and (b) Mo2Zn15 as a function of the distance from a Mo atom. The dotted lines show the experimental data and the solid lines are the fits.

The RDF curve for the $CaMoO_4$ reference is shown in Fig. 4. The first peak of RDF was fitted using a single scattering path, Mo−O at 1.771 Å (N=4), and S_0^2 = 0.92 and E_0 = 1.3 eV could be determined. In the Mo K-edge

EXAFS spectra of glass samples in which molybdate crystals were not formed, the second peak near 3.2 Å (the peak positions are not corrected for phase shift effects) corresponding to the actual path Mo−Ca at 3.69 Å and Mo−Mo at 3.87 Å was not observed. Mo ions were surrounded by 4.2 oxygen atoms at a distance of 1.78 Å whether or not crystals were formed.

4. Conclusions

The borosilicate glasses containing ZnO have been proposed to improve the solubility of MoO_3 in the glass. ZnO could effectively improve the solubility of MoO_3 in the borosilicate glasses and inhibited molybdate crystallization. In the glasses prepared in this study, XAS analysis determined that Zn and Mo were present in a tetrahedral structure.

REFERENCES

[1] S. Gin et al., An international initiative on long-term behavior of high-level nuclear waste glass, *Mater. Today* 16 (6) (**2013**) 243–248.
[2] A. Goel et al., Challenges with vitrification of Hanford High-Level Waste (HLW) to borosilicate glass – An overview, *J. Non-Crystalline Solids X* 4 (**2019**) 100033.
[3] S. Schuller, O. Pinet, and B. Penelon, Liquid–Liquid Phase Separation Process in Borosilicate Liquids Enriched in Molybdenum and Phosphorus Oxides, *J. Am. Ceram. Soc.* 94 (2) (**2011**) 447–454.
[4] S. Achigar et al., Dismantling nuclear waste rich in P2O5, MoO3 and ZrO2: How do these oxides incorporate in aluminoborosilicate glasses?, *J. Nucl. Mater.* 544 (**2021**) 152731.
[5] J. Neeway et al., Dissolution mechanism of the SON68 reference nuclear waste glass: New data in dynamic system in silica saturation conditions, *J. Nucl. Mater.* 415 (1) (**2011**) 31–37.