Phase Separation and Crystallization Induced by the Addition of Mo and P to a Calcium-Sodium Silicate Glass

S. Schuller, F. Bart
CEA Valrhô, DIEC/SCDV/LEBM, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

Silicate glasses with high molybdenum and phosphorus concentrations are partially crystallized. Their microstructure reveals the contribution of phase separation and crystallization phenomena during cooling. We investigated these phenomena in a simple calcium-sodium silicate glass and in glass compositions modified by adding variable quantities of phosphorus (up to 5 wt%) and molybdenum (up to 12 wt%). Various cooling scenarios were tested for each composition: quenching in water or on a stainless steel plate, or very slow cooling. The resulting glass specimens were then characterized by scanning electron microscopy, X-ray diffraction and differential thermal analysis to correlate the microstructure with the cooling rate according to the glass composition. The results show that phase separation and crystallization occur successively. The roles of molybdenum and phosphorus in this type of glass were identified: molybdenum favors phase separation, while phosphorus contributes to both phase separation and crystallization.

Introduction

Molybdenum and phosphorus are two elements that may be found in containment glasses for fission products generated by reprocessing spent fuel. The presence of these elements at high concentrations in silicate glasses could result in heterogeneities affecting the glass composition and microstructure. In order to understand the mechanisms involved, we investigated a calcium-sodium silicate glass system to which variable quantities of Mo and P were added. One of the test compositions containing both Mo and P was subjected to various cooling rates. The glass specimens obtained were characterized by scanning electron microscopy, by transmission electron microscopy coupled with electron microdiffraction analysis, and by X-ray diffraction analysis. On the basis of the results obtained, possible mechanisms were proposed to account for the role of each of these elements.

Experimental

Glass Compositions Investigated

A ternary calcium-sodium silicate glass system was selected as the basic experimental matrix. A glass composition outside the phase separation range[1] was prepared at 1400°C (SNC glass). Variable quantities of Mo and/or P were then added to the glass matrix (Table I).

Table I. Experimental Glass Compositions (oxide wt%). **M*x***: glass with Mo alone; **P*x***: glass with P alone; ***x***: weight percentage of MoO_3 or P_2O_5; **MP**: glass with 12% MoO_3 and 3.6% P_2O_5

Designation	SiO_2	Na_2O	CaO	MoO_3	P_2O_5
SNC	65.1	20.7	14.2	0	0
M1	64.5	20.5	14.1	1.0	0
M3	63.2	20.0	13.8	3.0	0
M5	61.9	19.6	13.5	5.0	0
M12	57.3	18.2	12.5	12.0	0
P1	64.5	20.5	14.1	0	1.0
P3	63.2	20.0	13.8	0	3.0
P5	61.9	19.6	13.5	0	5.0
P12	57.3	18.2	12.5	0	12.0
MP	55.0	17.4	12.0	12.0	3.6

Glass Fabrication Conditions and Cooling Scenarios

The glass samples were melted in a platinum crucible in a muffle furnace at 1400°C and refined for 3 hours. The samples containing P or Mo alone were either poured onto a metal plate or into an alumina crucible and annealed for 1 hour at 540°C. Three cooling scenarios were used for the MP glass: fast cooling by quenching in water, quenching in air by pouring onto a metal plate, and very slow cooling in an alumina crucible in three steps (the glass was cooled from 1400°C to 1000°C at a rate of 20°C/h, maintained for 40 hours at 1000°C, then allowed to cool to room temperature in the furnace).

Characterization Methods

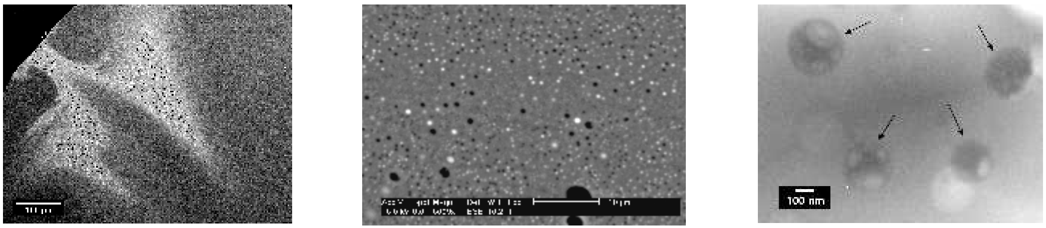
The glass samples were observed with a binocular magnifier or an optical microscope in polarized light. Only the glasses with visible heterogeneities were characterized. The first characterization step used a scanning electron microscope (SEM) with an energy-dispersive X-ray spectrometry (EDS) analyzer to determine the morphology and qualitative composition of the heterogeneities. The specimens were then analyzed by X-ray diffraction (XRD) to identify the phases. Some specimens were also analyzed by transmission electron microscopy (TEM) coupled with electron microdiffraction to determine the nature of phases well below 1 µm (as small as 100 nm).

Characterization Results

MP Glass

The MP glass melt containing both phosphorus and molybdenum was subjected to three different cooling rates.

MP glass quenched in water formed filaments as it was poured. Polarized optical microscopic observation revealed milky white zones extending along the filament centerline and a matrix with a different diffraction index. The milky zones (Figure 1a–1b) contained beads with diameters ranging from 100 nm to 1 µm, with a high average atomic number. In the clear-field TEM image (Figure 1c) the beads appear as dark zones. Inside the beads, lighter oval-shaped phases with lower atomic numbers are visible. The compositions of a few beads near one micrometer in size and the composition of the surrounding matrix were determined (Table II): the heterogeneities were highly enriched in Mo and slightly richer in P than the residual matrix, and also contained silica. XRD analysis revealed low diffraction peaks corresponding to $Na_2MoO_4,2H_2O$ crystals superimposed on two diffuse halos XRD (Figure 2). However, electron diffraction analysis showed that these heterogeneities diffracted electrons: the diffraction diagrams correspond to a single crystalline phase. These findings indicate that the beads probably consist of a mixture of phases: a vitreous phase of lower density than the surrounding matrix, and a much denser, Mo-enriched crystalline phase.



Backscattered electron SEM image (a) Backscattered electron SEM image (b) Clear-field TEM image (c)

Figure 1. Electron microscope images of MP glass quenched in water

Table II. Semi-quantitative EDS analysis results

Oxide wt%	Na_2O	SiO_2	CaO	MoO_3	P_2O_5
Spherical heterogeneities	16.2	23.6	10.2	44.9	4.6
Matrix	16.8	62.0	12.7	4.9	3.4

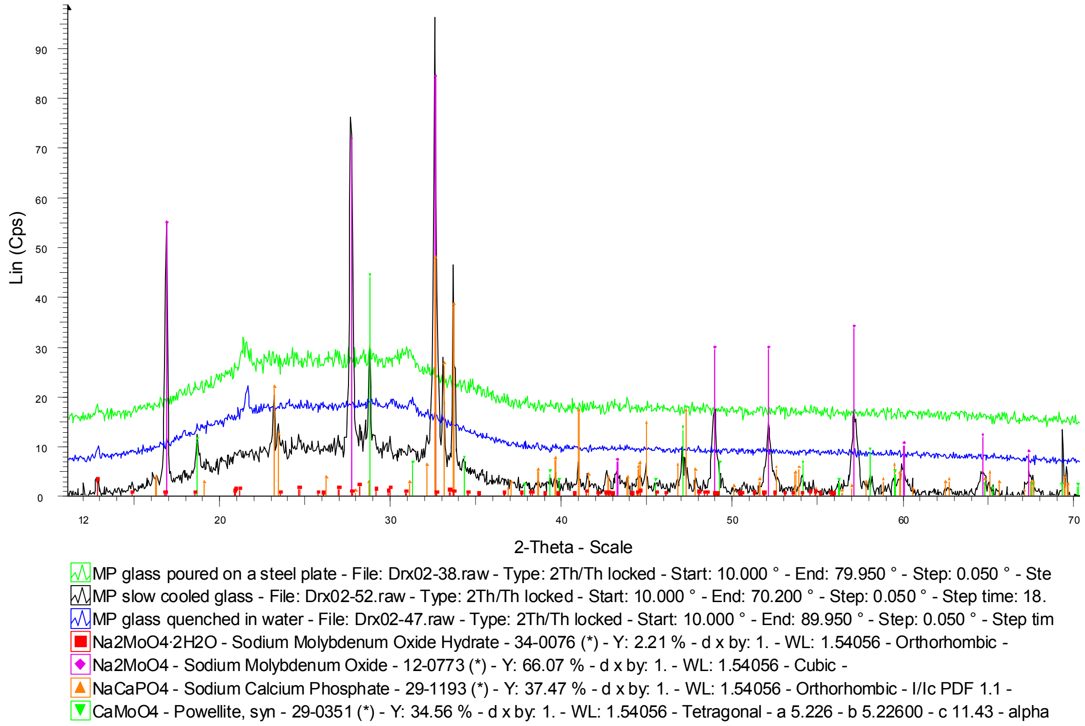


Figure 2. MP glass diffraction diagrams for tested cooling scenarios (opalescent vitreous phases)

The MP glass poured onto a steel plate underwent macroscopic phase separation during cooling. A whitish phase more dense than the glass appeared beneath an opalescent vitreous phase. XRD analysis of the whitish phase revealed a mixture of crystalline phases: mainly $Na_2MoO_4{,}2H_2O$ with minority $CaMoO_4$ and $NaCaPO_4$ phases. The opalescent vitreous phase exhibited the same facies as the glass quenched in water: milky zones containing beads not exceeding one micrometer in diameter, enriched in P and Mo. XRD analysis revealed low diffraction peaks corresponding to $Na_2MoO_4{,}2H_2O$ crystals superimposed on two diffuse halos (Figure 2).

Like the sample poured onto the steel plate, the MP glass subjected to very slow cooling separated into two distinctly different phases: a whitish phase denser than the glass and an opalescent vitreous phase (Figure 3a). The opalescent phase was identified by XRD analysis as containing Na_2MoO_4, $Na_2MoO_4{,}2H_2O$, $NaCaPO_4$ and $CaMoO_4$ phases (Figure 2). The opalescent vitreous phase included large numbers of white nodules about 200 µm in diameter, containing several types of crystals. The predominant crystalline phase was Na_2MoO_4 (Figure 3c), which is water-soluble[a]. Dipyramidal square-base $CaMoO_4$ crystals ranging in size from 10 to

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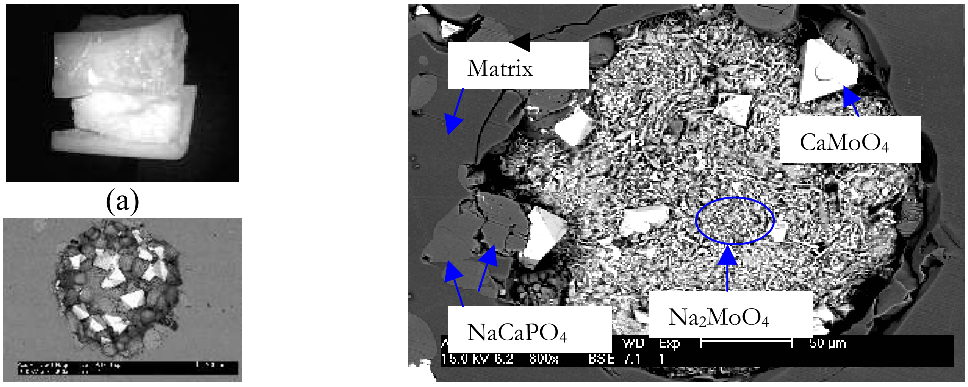
[a] When fully solubilized phases are polished under water, the surface is pitted where the crystalline phases are absent (Figure 3b).

100 µm were distributed within the nodules. Rounded $NaCaPO_4$ crystals (10–80 µm) were observed at the interface between the glass matrix and the sodium molybdate crystals. TEM observation showed that the large crystallized nodules were surrounded by small beads identical to those observed in the water-quenched glass, and which also diffracted the electron beam.



(a)

(b)

(c)

Figure 3. Images of MP glass after very slow cooling

Glass with Mo or P additive

The homogeneity of the SNC glass was not affected by adding up to 3 wt% MoO_3 and 5 wt% P_2O_5. The glass became opalescent (Figure 4) when larger quantities were added (M5, M12 and P12 glass specimens).

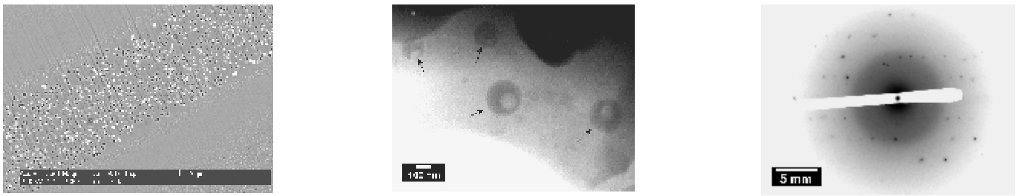
P12 – Opalescent vitreous phase
(a)

M12 – Opalescent vitreous phase
(b)

M12 – Crystallized phase
(c)

Figure 4. Binocular magnifier images (×10)

The glass containing 12 wt% phosphorus (P12) was highly opaque, showing broad milky-white veins under a binocular magnifier (Figure 4a). X-ray diffraction analysis revealed a high density of mixed sodium and calcium phosphate crystals ($NaCaPO_4$). Macroscopic phase separation was observed to a greater extent in the glass specimens containing only Mo than in those containing both Mo and P. After cooling, an opalescent vitreous phase separated by a denser crystallized white phase was observed in the M12 specimen (Figure 4b and 4c). XRD analysis of the crystallized white phase showed a predominant $Na_2MoO_4,2H_2O$ crystalline phase with minor $CaMoO_4$ and $Na_2Mo_2O_7$ phases. The opalescent phase in the M12 glass specimen included milky zones in curved planes within a translucent matrix. SEM analysis of these zones (Figurea) showed numerous submicron spherical heterogeneities or beads with a mean diameter of about 0.25 µm. Under TEM observation (Figureb), these beads showed the same characteristics as those observed in the water-quenched MP glass. The diffraction diagrams (Figurec) correspond to one or more monocrystals.



Backscattered electron SEM image (a) Clear-field TEM image (b) Electron microdiffraction diagram (c)

Figure 5 SEM and TEM characterization of M12 glass

Discussion

This experimental work addresses three aspects:

- the respective roles of phosphorus and molybdenum in phase separation and crystallization,
- the stable or metastable nature of phase separation,
- the type of phase separation mechanisms: nucleation and growth, or spinodal decomposition[2].

Mo or P added separately exhibited different behavior in the calcium-sodium silicate matrix. Phosphorus alone resulted in opacification of the glass matrix due to the crystallization of $NaCaPO_4$ without prior phase separation. Adding molybdenum alone resulted in significant macroscopic phase separation followed by crystallization of the separated phases. Adding both P and Mo tended to diminish the macroscopic phase separation and increase the crystallization of $NaCaPO_4$.

The microstructure of the MP glass depended on the cooling scenario. Water quenching induced phase separation followed by partial crystallization of the separated phases. Air quenching resulted in macroscopic phase separation, with a crystallized phase appearing during cooling; the vitreous phase of this glass was morphologically similar to the water-quenched glass, but greater crystallization of the separated phases occurred. Glass subjected to very slow cooling included large entirely crystalline nodules comprising a mixture of three clearly identified phases: Na_2MoO_4, $CaMoO_4$ and $NaCaPO_4$.

Examination of the glass specimens showed that phase separation and crystallization occur successively: liquid-liquid phase separation is followed by crystallization within the separated phases. Phase separation can occur above the melting temperature as a stable phenomenon, or below the melting point as a metastable phenomenon[3]. Although the occurrence of macroscopic phase separation suggests that the separation was stable in this case, this observation is not sufficient to resolve the issue since, if quenching is too mild, metastable phase separation can occur in the subliquidus domain.

Regardless of the cooling scenario, the spherical heterogeneities ranging in size from 100 nm to 1 μm in all three glasses were dispersed in the macroscopically observed opalescent zones. These spherical phases showed little interconnection, and corresponded to a distinct interface. This morphology suggests that the phase separation phenomenon in these glasses is governed by a nucleation and growth mechanism rather than by a spinodal decomposition mechanism that would have resulted in greater interconnection of the separated phases.

Conclusion – Outlook

The investigation of a simple calcium-sodium silicate glass system containing variable quantities of Mo and P showed that phase separation and crystallization occurs successively in this type of system. The first step is phase separation in the glass: the morphology of the separated phases suggests that the phenomenon is the result of a nucleation and growth mechanism. Crystallization then occurs as crystals of different chemical compositions form within the separated phases: Na_2MoO_4, $CaMoO_4$ and $NaCaPO_4$. Mo and P additives revealed different behavior: Mo added alone at high concentrations in the calcium-sodium silicate glass favored phase separation, while P affected both crystallization and phase separation.

It is difficult to conclude regarding the stable or metastable nature of the phase separation. Very rapid quenching must be carried out to resolve this issue; this cooling scenario will also confirm whether crystallization occurs after phase separation.

Acknowledgments

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