Journal of Non-Crystalline Solids 457 (2017) 13–24

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Hafnium solubility determination in soda-lime aluminosilicate glass

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ARTICLE INFO

Article history:
Received 20 July 2016
Received in revised form 4 November 2016
Accepted 11 November 2016
Available online 27 November 2016

Keywords:
Hafnium oxide
Solubility
Aluminosilicate glass melt
Reducing conditions
Crystallization

ABSTRACT

The solubility of hafnium dioxide (HfO_2), used as a surrogate for tetravalent uranium, is measured in glass melts belonging to the CaO-Al_2O_3-SiO_2 and Na_2O-CaO-Al_2O_3-SiO_2 systems, under oxidizing and reducing conditions. Two methods have been carried out to determine it and the kinetic factors controlling the HfO_2 dissolution in glass melt have been investigated in order to approach equilibrium. The solubility ranges from 3 to 6.5 mol% HfO_2 in aluminosilicate glasses at temperature between 1250 °C and 1400 °C, and is not affected by the redox conditions. Conversely, the solubility is modified by the melting temperature and the glass composition. The excess of alkalis or alkaline earths which are not involved in the charge balance of AlO_4 tetrahedrons in the silica network appears to play a significant role. Glass homogeneity is checked by scanning electron microscopy and X-ray diffraction. HfO_2, $HfSiO_4$, $Ca_2HfSi_4O_{12}$, $Na_4Hf_2(SiO_4)_3$ and $Na_2HfSi_2O_7$ are metastable crystals observed in the glass melts. The stability of those crystalline phases mainly depends on the glass composition.

1. Introduction

1.1. Background

Reprocessing of the spent nuclear fuel generates High Level Waste (HLW) which contains fission products and actinides. To be immobilized, these HLW are incorporated at about 1100 °C in a borosilicate glass matrix. In the same way, Intermediate Level Waste (ILW) including both actinides and metals are planned to be confined by a vitrification process. The metallic fraction is melted with the glass melt at a higher temperature, between 1250 °C and 1400 °C, and the glass melt is expected to incorporate the actinides, uranium and plutonium mainly, in its silicate network. As boron is known to volatilize from borosilicate melts at high temperature [1], aluminosilicate glasses appear as better candidates for that process. Besides, the molten metal phase imposes a strongly reducing environment to the glass melt and thus impacts actinides oxidation state and consequently their solubilities. In highly reducing conditions, U^{IV} and Pu^{III} are the main forms expected in the melt [2,3]. Plutonium is more soluble in glass melted in reducing conditions (Pu^{III}) [2] while uranium is more soluble in oxidizing conditions (U^{VI}) [3]. Moreover, only few data about uranium solubility in glasses melted in reducing conditions are given in the literature [3–7] and fundamental data on uranium behavior in aluminosilicate glasses have to be investigated in such conditions.

This study presents characteristics of soda-lime aluminosilicate glasses containing tetravalent hafnium (Hf^{IV}) which is taken as a uranium surrogate for the reduced U^{IV} species. Hafnium is usually used as a surrogate for tetravalent plutonium (Pu^{IV}) [8–11]. Uranium and hafnium are both heavy elements and display quite similar ionic radii for a given coordination number. At low oxygen fugacities, as looked for in our strongly reductive conditions, tetravalent uranium (U^{IV}) is mainly expected in the melt. Preliminary results with hafnium are shown here, before a further study with uranium. The first objective of this work is to study hafnium incorporation into a glass-forming melt under reducing environment and to optimize the Hf-doped glasses elaboration conditions in order to approach equilibrium. The second objective is to determine hafnium solubility as a function of the melting temperature, the glass composition and the redox conditions. Hafnium crystallization is also investigated.

1.2. State of the art

The thermodynamic solubility of an element in the glass is the maximum concentration of this element that can be loaded in the glass network at a given temperature. To determine it, two methods are commonly used. The first one consists in gradually increasing the amount the element to incorporate in the glass until a heterogeneous phase appears in the system (crystallization or/and demixing) [12]. The second one is embodied in introducing the desired element in excess in the glass and measuring its concentration in the vitreous matrix [13,14]. That means the saturated glass melt shows lots of heterogeneities. To make a difference between the gradation and the saturation methods, we named the last one the saturation solubility (S_S). The

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.11.009
0022-3093/

issue of reaching the equilibrium is raised in both cases. To approach equilibrium, the system has to verify several conditions [15], and if not, a conditional solubility (S_C) can be introduced notably for the gradation method [2,10]. This solubility depends on the experimental conditions used by the authors and it may be lower than the thermodynamic solubility for the gradation method or higher for the saturation technique [16].

Most hafnium solubility studies are focused on borosilicate glasses. Lopez measured conditional solubilities in a borosilicate glass as function of the melting temperature [10]. At 1400 °C, hafnium conditional solubility was between 1.2 and 1.5 mol% HfO_2. Cachia [17] reported a higher conditional solubility at the same temperature, between 1.8 and 2.2 mol% HfO_2 in the same glass by modifying the experimental protocol. In the Na_2O-B_2O_3 system, Res [18] observed that increasing the Na_2O concentration improved the HfO_2 solubility up to 12 mol% HfO_2 at 1400 °C for a glass containing 18 mol% Na_2O. Nevertheless, droplet-like micro-heterogeneities were revealed by SEM in clear glasses. Feng [19] found that hafnium solubility in a sodium boro-aluminosilicate was positively related to the excess of Na_2O relative to Al_2O_3. At 1450 °C, the highest solubility measured in a Na-rich glass was 14.4 mol% HfO_2. Unfortunately, few information is given about the way of determining that solubility limit. The relationship between hafnium solubility and glass composition was also investigated by Davis [8]. He demonstrated that the solubility limit of HfO_2 in peralkaline glasses (Na_2O mol% > Al_2O_3 mol%) in the system SiO_2-Al_2O_3-B_2O_3-Na_2O was linearly and positively correlated with the molar $Na_2O/(Na_2O + Al_2O_3)$ ratio. The solubility of HfO_2 in these glasses ranged from 2 to 16 mol% at 1450 °C. This "peralkalinity effect" had been alike observed in B-free glass melts for +4 cations (such as Zr^{IV} and Ti^{IV}) [14,15,20]. In contrast, the mechanism for HfO_2 dissolution seems to be different in peraluminous glasses (Na_2O mol% < Al_2O_3 mol%). In the peraluminous melts, the HfO_2 measured solubility by Davis [8] is lower than 3 mol% and, B_2O_3 and Al_2O_3 may help to solubilize it. Ellison [20] showed that hafnium solubility decreased in B-free peraluminous melts in the system SiO_2-Al_2O_3-Na_2O-K_2O with the SiO_2 content increasing and measured solubility limits lower than 1 mol% HfO_2 in equilibrated liquids at 1400 °C. Above the solubility limit, the Hf-bearing crystallized phases were mainly monoclinic hafnia (HfO_2) [8,9,18] and occasionally hafnon ($HfSiO_4$) [10,20].

All these authors had melted their glasses under oxidizing conditions, namely in air and in Pt-Rh, ZrO_2 or Al_2O_3 crucibles.

2. Experimental and analytical procedures

2.1. General features

Hf solubility was determined in two simplified aluminosilicate glasses based on the industrial glass formulations A and B, A glass containing 22.33 mol% Na_2O while B being sodium free (Table 1) and for two bracketing temperatures (1250 °C and 1400 °C). Redox conditions during the Hf-doped glasses meting were changed using different types of crucibles and atmospheres. Platinum crucible (Pt-5%Au) and air atmosphere were used for oxidizing conditions, while pure graphite (C_g) or graphite and silicon carbide (C-SiC) crucibles and argon (Ar) atmosphere imposed reducing conditions. The C-SiC crucible (A5/0 Salamander Super, Morgan MMS) is a type of crucible frequently used in the metallurgy field. It is mainly composed of C_g, SiC, a mullite binder ($3Al_2O_3$-$2SiO_2$) and some impurities such as Fe_3Si. Ar atmosphere was used to prevent these crucibles from corrosion.

Table 1
Targeted chemical compositions of main glasses.

	Glass composition (mol%)				
Sample name	SiO_2	Al_2O_3	CaO	Na_2O	HfO_2
A	57.43	6.25	13,99	22.33	0
B	57.43	6.25	36.32	0	0
C	56.54	6.15	13.77	21.98	1.56

2.2. Glass fabrication

2.2.1. Starting glasses

The A and B glasses (Table 1) were prepared with the following commercial precursors: SiO_2 (Sifraco, 0.994); Na_2CO_3 (Sigma-Aldrich, 1); CaO (Aldrich, 0.999); Al_2O_3 (Sigma-Aldrich, 1). For the Na-rich A glass, a decarbonation step was previously performed at 850 °C for 6 h. Then, the mixed components (≈150 g) were melted at 1400 °C for 3 h in a platinum crucible (Pt-10%Rh), under air. Glass melts were then poured in stainless steel plate, milled and screened up to 400 μm particle size to be further used as starting glass materials for Hf-doped glasses. Milling was performed in a tungsten carbide (WC) vessel using WC balls (Planetary Ball Mill PM 200).

Hafnium was added as HfO_2 powder (Alfa Aesar, 0.999) and mixed with the former glass powders. Three different types of hafnium particle size were used: 15, 70 and 158 μm.

The particle size, expressed as the median value (d_{50}) and size distribution of powders were determined from the volume distribution measured by a laser granulometer (Malvern Mastersizer 3000) in ethanol.

C glass was formed by adding 1.56 mol% HfO_2 to the Na-rich glass (Table 1). This value of 1.56 mol% HfO_2 is a relevant content for the industrial process. Moreover, the hafnium solubility in glass melt should be higher than this value as referenced in Section 1.2.

2.2.2. Optimized protocol definition for Hf-doped glasses

The influence of different experimental parameters (HfO_2 particle size, fusions number, melting time and temperature) has been checked for the C glass elaboration in order to optimize the process (Table 2). The powder mixture (≈3 g) was melted in a C-SiC crucible under Ar atmosphere. After melting, the molten glass was cooled by shutting off the heat source (cooling rate < 8 °C/min). In case of several meltings, each remelting was preceded by a glass sample milling step (WC vessel and ball, Mixer Mill MM 200) to ensure its homogenization. Final glass samples were removed from the crucible and have roughly a 20 mm diameter and 6 mm height (Fig. 2). An optimized protocol was then defined for Hf solubility measurements. To minimize hafnium sedimentation and its heterogeneities, fine HfO_2 powders were used (15 μm particle size). Remeltings enabled to homogenize the whole glass melt. The 3 h run duration allowed avoiding bubbles and longer run duration did not really impact the HfO_2 dissolution and had the drawback of increasing the Na volatilization. Thus, the experimental procedure followed for solubility measurements comprised three meltings for 3 h at 1250 °C or 1400 °C with two intermediate glass millings (Fig. 1).

A and B glass powders were respectively mixed with different amounts of HfO_2, ranging from 1.56 mol% to 10 mol% HfO_2 in the final glass. The powder mixture was fused either in a Pt-Au crucible and air atmosphere (oxidizing conditions) or in a C-SiC (or C_g) crucible under Ar atmosphere (reducing conditions). Glasses were directly quenched in air (cooling rate about 100 °C/min) and then milled. The milling and remelting steps were done twice. Finally, the crucible was removed

Table 2
Glass elaboration parameters of 1.56 mol% HfO_2-doped glasses melted in C-SiC crucible.

Sample name	Glass elaboration parameters			
	Melting time	Melting temperature	HfO_2 particle size	Fusions number
C0	3 h	1250 °C	70 μm	1
C1	12 h	1250 °C	70 μm	1
C2	3 h	1400 °C	70 μm	1
C3	3 h	1250 °C	158 μm	1
C4	3 h	1250 °C	15 μm	1
C5	3 h + 3 h	1250 °C	70 μm	2
C6	3 h + 3 h + 1 h	1250 °C	70 μm	3