Nuclear Instruments and Methods in Physics Research B xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

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

Nanoscale imaging of alteration layers of corroded international simple glass particles using ToF-SIMS

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ARTICLE INFO

Article history:
Received 4 September 2016
Received in revised form 1 December 2016
Accepted 23 January 2017
Available online xxxx

Keywords:
ToF-SIMS
Nanoscale imaging
Glass corrosion
Alteration layer
ISG particles

ABSTRACT

Glass particles with dimensions typically ranging from tens to hundreds of microns are often used in glass corrosion research in order to accelerate testing. Two-dimensional and three-dimensional nanoscale imaging techniques are badly needed to characterize the alteration layers at the surfaces of these corroded glass particles. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) can provide a lateral resolution as low as ~100 nm, and, compared to other imaging techniques, is sensitive to elements lighter than carbon. In this work, we used ToF-SIMS to characterize the alteration layers of corroded international simple glass (ISG) particles. At most particle surfaces, inhomogeneous or no alteration layers were observed, indicating that the thickness of the alterations layers may be too thin to be observable by ToF-SIMS imaging. Relatively thick (e.g., 1–10 μm) alteration layers were inhomogeneously distributed at a small portion of surfaces. More interestingly, some large-size (tens of microns) glass particles were fully altered. Above observations suggest that weak attachment and the defects on ISG particle surfaces play an important role in ISG glass corrosion.

1. Introduction

In the nuclear power industry, vitrification is a method to treat the radioactive fission products that have been recovered after used fuel reprocessing [1]. Different glass forming and modifying additives will lead to different nuclear waste glasses [2]. Management of the resulting glass waste form typically calls for disposal in a geological repository. To protect the environment and humans, the long-term (geological time) stability of high-radioactive waste glasses is a requirement. Thus, understanding the corrosion behavior of the waste glasses is of great significance.

Borosilicate glasses are widely considered as the preferred matrix for radioactive waste immobilization [3]. Therefore, extensive efforts have been performed to understand corrosion mechanism of these glasses. However, due to differences in the composition of these glasses, the use of different experimental methods and the variety of analytical tools, which are needed in these studies, is often impractical to directly compare results from different research groups. This impedes a comprehensive understanding mechanism(s) responsible for glass corrosion.

To mitigate this problem, the six-component International Simple Glass (ISG) has been developed as a model system to understand the mechanisms of glass corrosion [3]. The glass composition was chosen because it has the most common components that exist in many borosilicate nuclear glasses and can be easily fabricated at a large scale. Also, the long-term corrosion rate was found to be most similar to that of the SON68 glass, the non-radioactive simulant glass that closely resembles the glass composition of R7T7 which is the waste glass currently produced by AREVA at La Hague, France. Through the production and distribution of this glass, results obtained by different groups can be well compared and related. Thus, a worldwide research campaign is currently underway to understand the corrosion behavior of ISG glass [4,5].

The studies involving corrosion of ISG are often conducted by using glass particles rather than coupons because the use of particles, which increases the surface area of the glass exposed to the corroding fluid, accelerates the corrosion of the glass. This allows for a relatively quick buildup of concentrations of glass components in solution, which allows for near-equilibrium conditions

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http://dx.doi.org/10.1016/j.nimb.2017.01.053
0168-583X/

to be quickly obtained. Additionally, the high surface area leads to the buildup of glass constituents in solution where the concentration is high enough to be measured through traditional solution analyses such as inductively coupled plasma techniques. Thus, the use of glass particles has led to a large collection of useful data [6–8].

In addition to monitoring the evolution of the contacting solution during corrosion testing, elemental mapping of the solids is critical to elucidate the behavior of chemical components in the alteration layers. Scanning electron microscope (SEM) combined with energy dispersed X-ray (EDX) analysis has been widely used for this [4,9]. However, SEM/EDX has two big disadvantages in glass corrosion research. First, the best lateral resolution of SEM/EDX is normally ~1 μm and, in many cases, better lateral resolution is needed and second, SEM/EDX is not sensitive to elements light elements such as boron, which is a very important glass modifying element present in many waste glasses [4].

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most surface-sensitive techniques. It is sensitive to most elements, including light elements such as boron, lithium and hydrogen and it can provide a lateral resolution of ~100 nm. Therefore, ToF-SIMS mapping has been employed in glass corrosion research in the last few years [4,10,11]. In this study, ToF-SIMS was used to characterize alteration layers of corroded ISG particles. An unexpected inhomogeneous corrosion behavior was observed for the first time, which may be attributed to the weak attachment of alteration layers on the particle surfaces and defects at the ISG particle surfaces.

2. Experimental

The ISG glass was supplied by MoSci (Rolla, MO, USA). The ISG glass is part of a large batch that was fabricated to be used in an international effort to reach a consensus on the mechanisms controlling the long-term glass dissolution rate. The sample was prepared by crushing the as-received glass and sieving to a −60 +40 mesh fraction (250–420 μm size). This grinded glass sample was washed with water, then ethanol, and dried in an oven at 90 °C. The composition of ISG is provided in the Table 1.

The corrosion experiment was performed by packing the glass in a Polyether ether ketone (PEEK) column. The column was saturated under vacuum with 18.2 MΩ cm DI (deionized) H_2O at ambient temperature and then allowed to desaturate by gravity drainage with the gas pressure being brought to the desired level. The column was heated to 90 °C at which point the influent valve was opened, and influent was set to a flow rate of 2 mL d^{-1}. The glass was allowed to corrode in unsaturated conditions for a duration of six months. After termination of the experiment, solid samples were collected from the column at various depths (~0.48 cm/section, totally 16 sections) to monitor the evolution of phases along the depth of the column. A schematic illustration of the system used for corrosion experiment was shown in Fig. 1.

For ToF-SIMS analysis, the corroded ISG glass particles were mounted with EpoThin™ 2 epoxy resin and then the samples were cut and polished for SEM and ToF-SIMS analysis. The details of the preparation procedure are shown in Fig. 2 (a): (1) ~5 mg of ISG particles were added on an optical glass slide (~1 mm thick, 10 × 10 mm^2 size) surface, and then ~0.1 mL of mixed epoxy

Table 1
The nominal components of ISG glass (mol%).

SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
60.2	16.0	12.6	3.8	5.7	1.7

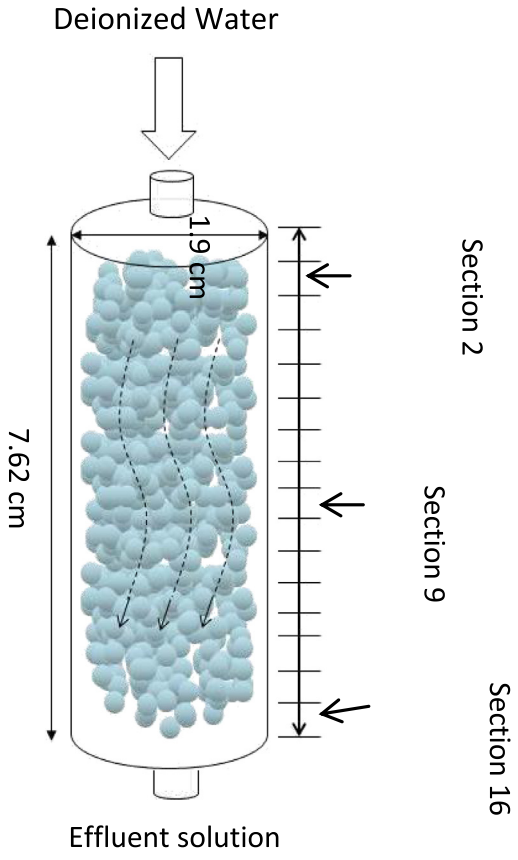

Fig. 1. A schematic illustration of the system used for corrosion experiment.

(2:1 in weight for epoxy resin and epoxy hardener) was dropped on the glass particles. The slides were kept flat in the fume hood overnight and then transferred into a 50 °C oven for 3 h for a further cure. (2) Two slides were attached together using a plastic clip with the ISG particles at outsides, as shown in Figs. 2a-3. (3) The sample was moved into a silicone gel mold and a desirable amount of EpoThin™ epoxy was poured into the mold. (4) After cured, the epoxy bulk was cut into two pieces by a diamond saw to expose cross sections of the glass particles. (5) After mechanical polishing, the samples were ready for SEM and ToF-SIMS analysis. An optical photograph of a sample was shown in Fig. 2(b).

A Hitachi TM-1000 SEM instrument was used for SEM imaging. Before SEM measurement, a thin layer of carbon (~20 nm) was sputter coated on the sample surface to reduce the charging effect.

ToF-SIMS imaging was performed using a TOF.SIMS 5 spectrometer (IONTOF GmbH, Müster, Germany), which was equipped with a 25 keV bismuth (Bi) cluster ion source, a 20 keV Ar_n^+ ion source, and a 2 keV Cs^+/O_2^+ sputtering ion source. The SIMS imaging locations were selected based on SEM images to facilitate a direct comparison of SEM and SIMS images. Before SIMS imaging analysis, a 1 keV O_2^+ beam was scanned over a 300 × 300 μm^2 area for about 100 s to remove the carbon coating and possible surface contamination.

A 25 keV Bi^+ beam was used as the analysis beam. The Bi^+ beam was focused with a beam size of ~200 nm diameter and was scanned over a 50 × 50 μm^2 (or other desirable sizes ranging from 30 × 30 to 200 × 200 μm^2) area in the O_2^+ beam crater to collect ion images. All ion images were 256 × 256 pixels. The current of the pulsed Bi^+ beam was ~0.5 pA and the time for each measurement

Please cite this article in press as: J. Zhang et al., Nanoscale imaging of alteration layers of corroded international simple glass particles using ToF-SIMS, Nucl. Instr. Meth. B (2017), http://dx.doi.org/10.1016/j.nimb.2017.01.053