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Dilute condition corrosion behavior of glass-ceramic waste form

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HIGHLIGHTS

- Multi-phase glass ceramic (oxyapatite, powellite, cerianite, and borosilicate glass) formed on canister centerline cooling.
- Modified-single-pass-flow-through corrosion testing by solids analysis in dilute conditions.
- Enhanced crystal-glass interface corrosion resulting from mechanical stress inside unique oxyapatite cluster morphology.
- SIMS (light element) and STEM-EDS analysis of crystal-glass interface and corrosion.
- Corrosion rates of the waste form were controlled by the continuous phase, borosilicate glass.

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ABSTRACT

Borosilicate glass-ceramics are being developed to immobilize high-level waste generated by aqueous reprocessing into a stable waste form. The corrosion behavior of this multiphase waste form is expected to be complicated by multiple phases and crystal-glass interfaces. A modified single-pass flow-through test was performed on polished monolithic coupons at a neutral pH (25 °C) and 90 °C for 33 d. The measured glass corrosion rates by micro analysis in the samples ranged from 0.019 to 0.29 g m^{-2} d^{-1} at a flow rate per surface area = 1.73×10^{-6} m s^{-1}. The crystal phases (oxyapatite and Ca-rich powellite) corroded below quantifiable rates, by micro analysis. While, Ba-rich powellite corroded considerably in O10 sample. The corrosion rates of C1 and its replicate C20 were elevated an order of magnitude by mechanical stresses at crystal-glass interface caused by thermal expansion mismatch during cooling and unique morphology (oxyapatite clustering).

1. Introduction

Borosilicate glass-ceramics are being developed as a highly waste-loaded alternative to borosilicate glass for the immobilization of high-level waste (HLW) that will be generated by future aqueous reprocessing schemes (e.g., TRUEX) to recycle used nuclear fuel [1,2]. Borosilicate glass is a widely accepted waste form for immobilization of HLW that has been utilized by France, the United States, Great Britain, Germany, and Japan, because the glass structure can accommodate a wide range of fission products [3–9]. Some HLW components such as Mo, lanthanides (Ln), and noble metals (e.g., Pd, Rh, Ru) have limited solubility in the glass phase, leading to phase-separation and/or crystallization even at a relatively low waste loading of 18 mass% [1,10].

The goal for developing the glass-ceramic waste form as an alternative to borosilicate glass is to accommodate insoluble components and radioactive fission products into specific durable crystalline phases by tailoring the chemistry and cooling rates of the canistered waste form [1]. The targeted crystalline phases are powellite ($XMoO_4$; $X =$ alkali, alkaline earth, and/or Ln); oxyapatite ($Y_2Ln_8Si_6O_{26}$; Y = alkali and/or alkaline earth); cerianite ($Ce_xZr_{1-x}O_2$); pollucite ($Cs_xRb_{1-x}AlSi_2O_6$); and Ln-borosilicate ($Ln_3BSi_2O_{10}$). By targeting these phases, the waste loading is increased from ~20 mass% to between 45 and 55 mass% in the glass-ceramic waste form. The use of these targeted crystalline phases facilitates the high waste loading while accommodating the increased radioactive decay heat because of their thermal stability with respect to additional phase changes.

Glass ceramics present more challenges than a single-phase glass in terms of controlling phase chemistry and microstructure

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as well as understanding how each phase impacts waste form performance. The major goal is to produce a waste form that is chemically durable by consistently achieving the targeted phases, microstructure, and residual glass composition without creating a bulk glass or interface glass phase that have low chemical durability. In addition, the microstructure should to be controlled such that mechanical stresses are managed to avoid cracking/separation of the crystals from the glass phase.

Recent work has demonstrated that the targeted crystalline phases can be achieved over a range of chemistries, waste loadings, and slow-cooling rates in the laboratory [11]. In addition, one composition has been successfully processed with an engineering-scale cold-crucible induction melter, where the targeted glass-ceramic was achieved upon slow cooling in an engineering-scale canister [11]. A limited number of glass-ceramic compositions that were subjected to the product consistency test (PCT) [12] showed low normalized concentrations for B, Na, Li, Mo, and Si in solution (<0.8 g L^{-1}) for the bulk waste form in static conditions at 90 °C between 3 and 28 d [13].

In the work reported here, polished monolithic glass-ceramic coupons were subjected to a modified single-pass flow-through (MSPFT) corrosion test in a buffered solution at a neutral pH (25 °C), 90 °C, and with a flow rate per surface area (q/s) of 1.73×10^{-6} m s^{-1} for 33 d in dilute solution conditions. This allowed for the determination of bulk glass ceramic corrosion rates based on coupon mass loss. The bulk corrosion rates of the coupons as well as the corrosion rates of individual phases were determined by microanalysis of the coupons in cross section using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

Table 1
Glass-ceramic target and calculated[a] final glass compositions.

Component	Composition, mole fraction						
	C1 & C20 Start Glass	C1 Final Glass	C20 Final Glass	O10 Start Glass	O10 Final Glass	O16 Start Glass	O16 Final Glass
Al_2O_3	0.038	0.047	0.047	0.065	0.078	0.065	0.077
B_2O_3	0.113	0.142	0.140	0.080	0.096	0.080	0.118
CaO	0.085	0.043	0.044	0.060	0.019	0.140	0.101
Li_2O	0.033	0.041	0.040	0.000	0.000	0.060	0.089
Na_2O	0.041	0.048	0.047	0.090	0.105	0.020	0.021
SiO_2	0.477	0.525	0.525	0.520	0.572	0.440	0.433
MoO_3	0.042	0.000	0.000	0.037	0.000	0.039	0.004
SrO	0.015	0.005	0.005	0.013	0.002	0.013	0.011
BaO	0.022	0.028	0.028	0.019	0.023	0.020	0.030
Rb_2O	0.004	0.004	0.004	0.003	0.004	0.003	0.002
Cs_2O	0.016	0.020	0.020	0.014	0.016	0.015	0.009
Ce_2O_3	0.015	0.005	0.006	0.013	0.006	0.013	0.007
Eu_2O_3	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Gd_2O_3	0.001	0.001	0.001	0.001	0.001	0.001	0.001
La_2O_3	0.008	0.004	0.004	0.007	0.004	0.007	0.006
Nd_2O_3	0.024	0.009	0.010	0.021	0.010	0.022	0.015
Pr_2O_3	0.007	0.005	0.005	0.006	0.004	0.006	0.004
Sm_2O_3	0.005	0.004	0.004	0.004	0.004	0.004	0.005
Y_2O_3	0.004	0.004	0.004	0.004	0.003	0.004	0.004
ZrO_2	0.038	0.047	0.047	0.033	0.039	0.034	0.045
Others	0.014	0.017	0.017	0.012	0.014	0.013	0.019
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Waste Loading, mass%	47.4	26.2	27.0	41.9	24.4	44.6	23.8

[a] Final glass compositions calculated based on measured crystal fraction and crystal compositions, waste loading in final glass is the mass% of the total (glass + crystal phases).

2. Experimental setup

2.1. Fabrication

Glass-ceramics with target compositions shown in Table 1 were made as 500 g batches from reagent-grade oxides, carbonates, and boric acid and homogenized for 4 min in an agate milling chamber. The component listed as “Others” in Table 1 was composed of a mixture of reagent grade 0.017 PdO, 0.065 RhO_2, 0.167 RuO_2, 0.054 Ag_2O, 0.098 CdO, 0.084 SeO_2, 0.052 SnO_2, and 0.463 TeO_2, given in mole fraction. The “Others” component was a subset of waste components and varied accordingly with waste loading. Each batch was melted twice in a lidded Pt/10% Rh crucible between 1250 °C and 1450 °C for 1 h and quenched on an Inconel plate in air; between the first and second melts, the glass was ground in a tungsten carbide mill for 4 min. The quenched glass was then reheated to the melting temperature for 30 min and slowly cooled down to 400 °C, based on the centerline cooling temperature profile of a 0.61-m (2-ft) diameter canister [14]. The phase assemblages of the slow-cooled glass-ceramic samples were characterized by XRD and SEM-EDS.

2.2. X-ray diffraction

X-ray powder diffraction was performed to determine the crystalline phases and their concentrations in the slow-cooled glass-ceramic specimens. Specimens were prepared for XRD by grinding them to a very fine powder and doping the powder with a known concentration (mass%) of Standard Reference Material #674b (TiO_2, rutile) to facilitate phase quantification including the amorphous fraction [15]. The XRD patterns were collected with a Bruker D8 Advance XRD system (Bruker AXS, Madison, WI) equipped with a Cu target ($K_{\alpha 1} = 0.15406$ nm) over a scan range of 5–75° 2θ using a step size of 0.015° 2θ and a hold time of 4-s per step. The scans were analyzed with TOPAS (v4.2) whole-pattern-fitting software according to the fundamental parameters approach [16]. Structure patterns were selected from the Inorganic Crystal Structure Database (release 2013) with unit cell dimensions refined during the fitting process of each pattern. The amorphous content of each specimen was determined by difference after crystalline phases were quantified and renormalized based on the concentration of the known internal standard (rutile).

2.3. Modified single-pass flow-through test

Modified single-pass flow-through tests were performed on a set of slow-cooled glass-ceramic coupons. Corrosion experiments were conducted using the MSPFT apparatus shown in Fig. 1 [17]. A syringe pump (Norgren Kloehn; Las Vegas, NV) was used to pump the buffered solution from the input reservoir to the reactor vessel inside the oven through Teflon® tubing. The Teflon reactor was a two-piece system consisting of the reactor base threaded together with the lid containing the inlet and outlet ports. The reactor had a diameter of 85 mm and a height of 121 mm, giving a total inner volume of 500 mL. The effluent solution then flowed out of the reactor to a collection bottle placed outside of the oven. The buffered solution was 0.05 M THAM hydroxymethyl-aminomethane adjusted to pH 7 (at 25 °C) through the addition of concentrated HNO_3.

The coupons were sectioned and polished on both sides to a final finish of 0.25 μm before beginning the experiment. The polished surface was masked at three locations, ~2 mm in diameter, with silicone sealant (Loctite 595 Silicone Sealant, Düsseldorf, Germany) to provide three reference points to the pristine starting coupon surface for measurements of alteration layer thickness by