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The effect of pre-treatment parameters on the quality of glass-ceramic wasteforms for plutonium immobilisation, consolidated by hot isostatic pressing

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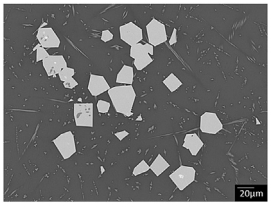
HIGHLIGHTS

- Optimisation of pre-treatment parameters for HIP glass-ceramics was investigated.
- Entrained porosity was minimised by *ex-situ* bake-out of oxide precursors at 600 °C.
- Phase assemblage and microstructure proved independent of bake-out parameters.
- Use of glass-frit precursor further improved process s throughput and simplification.

GRAPHICAL ABSTRACT



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ABSTRACT

Glass-ceramics with high glass fractions (70 wt%) were fabricated in stainless steel canisters by hot isostatic pressing (HIP), at laboratory scale. High (600 °C) and low (300 °C) temperature pre-treatments were investigated to reduce the canister evacuation time and to understand the effect on the phase assemblage and microstructure of the hot isostatically pressed product. Characterisation of the HIPed materials was performed using scanning electron microscopy (SEM), coupled with energy dispersive X-ray analysis (EDX) and powder X-ray diffraction (XRD). This analysis showed the microstructure and phase assemblage was independent of the variation in pre-treatment parameters. It was demonstrated that a high temperature pre-treatment of batch reagents, prior to the HIP cycle, is beneficial when using oxide precursors, in order to remove volatiles and achieve high quality dense materials. Sample throughput can be increased significantly by utilising a high temperature *ex-situ* calcination prior to the HIP cycle. Investigation of glass-ceramic wasteform processing utilising a glass frit precursor, produced a phase assemblage and microstructure comparable to that obtained using oxide precursors. The use of a glass frit precursor should allow optimised throughput of waste packages in a production facility, avoiding the need for a calcination pre-treatment required to remove volatiles from oxide precursors.

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1. Introduction

Hot Isostatic Pressing (HIPing) is a process which simultaneously applies heat and pressure to consolidate and sinter materials. The use of isostatic pressure during consolidation, applied using an inert gas, promotes densification, eliminating internal porosity. The potential benefits of HIPing are increasingly being recognised for the processing of radioactive wastes to produce passively safe wasteforms. The UK's Nuclear Decommissioning Authority (NDA) has identified HIP as a potential method for treating plutonium residues at the Sellafield site [1,2]. The UK's policy for dealing with the large PuO_2 stockpile at Sellafield is to fabricate MOx fuel, however, a recent analysis has highlighted the need to adopt a dual track approach to plutonium management with parallel development of a stockpile disposition pathway [3]. Aside from the potentially reusable plutonium stockpile, approximately 0.5 tonnes of material is not economically viable for reuse and has been identified as waste [4]. These Pu-residues are classified as higher activity waste due to the Pu content exceeding that of plutonium contaminated material wastes.

Zirconolite glass-ceramics are an attractive matrix for the immobilisation of low purity plutonium residues, which may also contain glass forming contaminants. In these materials, plutonium and other actinides are targeted for incorporation within the ceramic phase zirconolite, prototypically $CaZrTi_2O_7$, by substitution of the Ca and/or Zr sites. This phase has been demonstrated to exhibit exceptional stability toward aqueous dissolution and radiation damage required for geological disposal [5]. The glass phase provides the wasteform with the flexibility to accommodate the impurities associated with the plutonium feedstock [5]. In addition, the presence of a liquid glass phase during high temperature processing assists in the densification of the wasteform product.

Hot isostatic pressing is a highly flexible process with a large operating window, allowing effective processing of different wastestreams and different immobilisation matrices without the challenges associated with vitrification. Process control is simplified by processing the waste in hermetically sealed canisters, hence no off-gas is produced during the HIP cycle, and clearly, there is no requirement to pour or discharge the product, as in a melter system. The utilisation of a batch process enables robust plutonium accountancy, an important aspect for criticality and safeguards concerns. Actinide loadings in zirconolite based glass-ceramics exceed those observed in vitrified wasteforms, enabling higher actinide loadings and a reduced number of wasteforms for processing [6–8]. Coupling this with the significant volume reduction per waste package achieved during the HIP process (up to 60% volume reduction), there are potentially significant cost savings associated with the lifetime waste management costs.

Successful processing of radioactive wastes by HIPing typically requires the waste and glass/ceramic forming precursors to be dried and mixed before being packed into a stainless steel canister. The canister is evacuated at room temperature *via* an evacuation tube in the lid. Elevated temperatures may also be applied during this evacuation, in a process commonly referred to as a "bake-out" step [9]. A bake-out step is utilised to remove water and other volatiles from inside the canister, which could inhibit densification and create porosity in the final wasteform. The selection of glass/ceramic forming precursors is important to minimise the addition of potential volatiles in the HIP canister, hence metal carbonates and hygroscopic reagents are typically avoided (as in this study). When an acceptable vacuum is achieved, typically <25 Pa, the evacuation tube is crimped and sealed by welding. This paper highlights the importance of optimising the in-canister evacuation and bake-out process to achieve high quality, dense glass-ceramic products. The time taken to evacuate each canister could severely limit the operational throughput of a waste treatment plant utilising HIP technology, hence it is important to optimise the process at a laboratory scale before scaling up to full size HIP canisters.

With the aim to improve sample throughput whilst maintaining sample quality and reproducibility, we investigated the use of a waste/precursor *ex-situ* calcination step as an alternative or supplement to the in-canister bake-out on laboratory scale 30 ml canisters. The final wasteform microstructure and phase assemblage are discussed with respect to the pre-treatment parameters, as well as the final densities and time taken for each canister evacuation.

2. Experimental

Our target glass-ceramic phase assemblages for UK plutonium disposition are zirconolite $CaZrTi_2O_7$ distributed within a sodium aluminoborosilicate glass matrix. The materials fabricated in this study were formulated prior to optimisation of the glass-ceramic formulation and comprise zircon – $ZrSiO_4$ as the dominant crystalline phase, accompanied with other minor crystalline phases as described below. Although these materials do not comprise the optimised phase assemblage, they are considered to be a valid and useful test bed to understand the impact of pre-treatment parameters on the behaviour of the glass/ceramic precursors. The effectiveness of the *ex-situ* calcination and/or in-canister bake-out step on the quality of the wasteform product was judged on the basis of the wasteform phase assemblage, microstructure and entrained porosity. Table 1 lists the oxide precursors used to fabricate the glass-ceramic wasteforms in this study. The high glass fraction and high B_2O_3 content result in the stabilisation of zircon as the major crystalline phase as noted above and described in our previous study [10].

Powder samples were batched to a 70:30 wt % ratio of glass to ceramic with the target glass phase, $Na_2Al_{0.5}B_{1.5}Si_6O_{16}$. The batches were mixed in a planetary mill at 500 rpm for 5 min with isopropanol as a milling agent. The dried batches were packed and sealed into stainless steel HIP cans (approximately 36 × 38 mm (h x d)).

All samples were heat treated to remove volatiles. Samples underwent an *ex-situ* calcination prior to canister packing, an in-canister bake-out or a combination of the two. The pre-treatments for each sample are given in Table 2. For the calcinations, the batched and milled powders were heated for 16 h in an alumina crucible in a muffle furnace, the in-canister bake-outs were performed on the filled HIP canisters whilst under vacuum.

Sample E was fabricated using a glass frit precursor to compare against the use of oxide precursors. Sample E was batched with the same glass to ceramic fraction (70:30 wt %) and used a frit of the same target glass composition, $Na_2Al_{0.5}B_{1.5}Si_6O_{16}$, instead of the glass forming oxide reagents. The glass frit was produced by melting stoichiometric quantities of $Na_2B_4O_7$, Al_2O_3 and SiO_2 at 1500 °C for 5 h before pouring through a stainless steel mesh into

Table 1
Raw reagents used and their corresponding weight percentages for a 70:30 wt % glass: ceramic mix.

	Reagent	Wt. %
Glass formers	SiO_2	45.2
	Na_2SiO_3 – anhydrous	10.6
	Al_2O_3	3.60
	$Na_2B_4O_7$ – anhydrous	10.6
Ceramic formers	$CaTiO_3$	12.0
	TiO_2	11.0
	ZrO_2	7.00