The Consolidation of Glass-Ceramic Wasteforms by Hot Isostatic Pressing: Sample Optimisation – 16581

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ABSTRACT

Zirconolite based glass-ceramics were developed for the disposition of plutonium residues at the UK's Sellafield site. Glass-ceramics act as double barrier systems, separating Pu into a durable ceramic phase and retaining miscellaneous material in the amorphous phase. Here we discuss the optimisation of processing parameters and formulations of these alternative wasteforms. All samples were HIPed at 1250 °C, 100 MPa for 4 hrs. By investigating the effects of different pre-HIP heat treatments on sample quality and throughput, and glass phase compositions on the crystalline phase assemblage, an optimised method and wasteform composition were achieved.

INTRODUCTION

The UK has in excess of 100 tonnes of PuO_2 stored at the Sellafield site. Glass-ceramics were initially developed for the immobilization of the Pu-residues which are not economical for reuse as fuel, and are now being considered for the potential disposition of bulk PuO_2. Glass-ceramics are an attractive matrix for Pu immobilization as they can incorporate higher waste loadings than glass wasteforms, whilst maintaining an ease of processing. Excellent immobilization of Pu is reported and these wasteforms have lower dissolution rates than their vitrified equivalents.[2] Glass-ceramics act as double barrier systems by partitioning actinides into the more durable ceramic phase and retaining miscellaneous material in the glass phase. Zirconolite, $CaZrTi_2O_7$, is a ceramic phase known for its use in Synroc. It is a naturally occurring mineral and exhibits excellent durability and radiation tolerance properties desired for a HLW wasteform. Zirconolite readily accepts actinides and rare earth elements into its structure and natural analogues show excellent radionuclide retention even after amorphisation.[3]

In the zirconolite based glass-ceramic systems being developed in this project, the crystalline phase assemblage changes as a function of the glass phase composition.[4] This paper discusses the effect of aluminium concentration and glass fraction on the crystalline phase assemblage, such that a higher aluminium content favours a higher yield of zirconolite.

Hot Isostatic Pressing (HIPing) is a consolidation technique proposed to process glass-ceramic wasteforms for plutonium residue immobilisation.[5] Originally

developed for the diffusion bonding of fuel elements in nuclear submarines, hot isostatic pressing now has many applications for multiple industries and materials including aerospace and defence, metals and ceramics.[6] The flexibility of the technique makes it attractive for processing complicated waste-streams where current vitrification techniques are inapplicable and reprocessing is economically unviable. The high complexity and variability in the physical and chemical properties of plutonium residues can be easily accommodated using HIPing. Glass, ceramic, glass-ceramic and metallic wasteforms can all be processed with minimal changes to processing parameters, allowing the matrix to be designed around the waste, not around the method of immobilisation. HIPing achieves high density wasteforms by applying heat and pressure simultaneously. The use of both conditions allows lower consolidation temperatures to be used, and achieves dense wasteforms with finer grain structures, thus improving the durability and strength. Additionally, HIPing produces hermetically sealed wasteforms, which results in a uniform incorporation of radionuclides in the structure, at a significantly lower volume than equivalent cementitious wasteforms, ready for long-term storage.[7]

The waste and precursors are homogenously mixed and packed into stainless steel canisters, which are evacuated to ensure complete compaction and no porosity in the final product. During the evacuation process, the temperature is increased to bake-out the canister to remove any volatiles from inside, which would ultimately liberate during the HIP cycle and result in a poor wasteform. This process is the rate limiting step for sample throughput, taking up to 24hrs per canister and reducing process efficiency dramatically. A sample matrix investigated the effect of calcining the raw materials in a furnace overnight as opposed to the in-canister bake-out. It was envisaged, the overnight treatment would improve sample through-put without compromising on sample quality. Results demonstrated the importance of a high temperature heat treatment when using oxide precursors to achieve high quality HIPed materials. It should be noted this matrix was batched as a worst case scenario to investigate the experimental parameters, thus little/no zirconolite is expected to form due to reduced levels of aluminium.

METHOD
Processing Matrix
The powders were batched to a 70/30 wt% glass to ceramic with target glass phase being $Na_2Al_{0.5}B_{1.5}Si_6O_{16}$. The batches were packed into stainless steel canisters (approximately 36x38mm (h x d)), heat treated and evacuated, before being sealed ready for HIPing. Samples either underwent a high temperature (600 °C) overnight calcination or in-canister bake out, according to Table 1. Sample A had a low temperature heat treatment and was expected to attain a porous product due to incomplete removal of volatiles. Samples were HIPed at 1250 °C, 100 MPa with a 4 hr

dwell. The processed materials were analysed using a Hitachi TM3030 analytical scanning electron microscope (SEM) at a 15 kv accelerating voltage and a working distance of 8 mm. Samples were ground and sieved to <106 µm for X-ray diffraction (XRD) by using a Bruker D2 PHASER desktop diffractometer between 10° < 2θ < 70° (Cu Kα radiation and a position sensitive detector).

Table1. Sample matrix and individual sample heat treatments.

Sample	Heat treatment	
	Calcine (°C)	Bake out (°C)
A	0	300
B	0	600
C	600	300
D	600	0

Formulation Matrix

A second matrix of samples investigating the effect of glass fraction and composition on the crystalline phase assemblage were fabricated with varying aluminium concentrations, according to the target glass phase $Na_2Al_{1+x}B_{1-x}Si_6O_{16}$, where $x=0$, 0.2, 0.4, 0.6, 0.8, 1.0, and increasing glass fractions; 30 wt%, 50 wt% and 70 wt%. All samples were prepared and HIPed as stated above and were analysed by SEM and XRD.

RESULTS

Processing Matrix

Scanning electron microscopy (SEM) analysis of samples A-D (Table 1, Figure 1) showed microstructures with large zirconium-rich crystals and a smaller titanium-rich phase distributed in a glass matrix. As expected, sample A had a high level of porosity (visible by eye) and sample B showed no evident porosity. The microstructure and spatially resolved composition of the calcined samples C and D are indistinguishable from those of samples not subject to calcination at 600 °C (A & B). Unlike sample A, samples C and D have no visible porosity, which implies the addition of a calcination step was broadly similar to increasing the bake out temperature, removing volatiles without affecting the final product (Figure 1). XRD data (not shown) for each sample showed the same phase assemblage for all samples with the major phase identified as zircon (pdf-card 01-071-0991) and minor phase rutile (pdf-card 01-078-4188). To effectively study the effect of the pre-HIP parameters the sample matrix was batched with a high amount of the hygroscopic reagent borax ($Na_2B_4O_7$ – anhydrous). As a result the region of the phase diagram targeted is such that no zirconolite was expected to form. The overnight calcination significantly reduced the time taken per sample for evacuation, which ultimately increases the overall efficiency of the HIP process. It was decided to move forward with the overnight calcination and low

temperature bake-out for better sample throughput and to ensure sample quality on future samples.
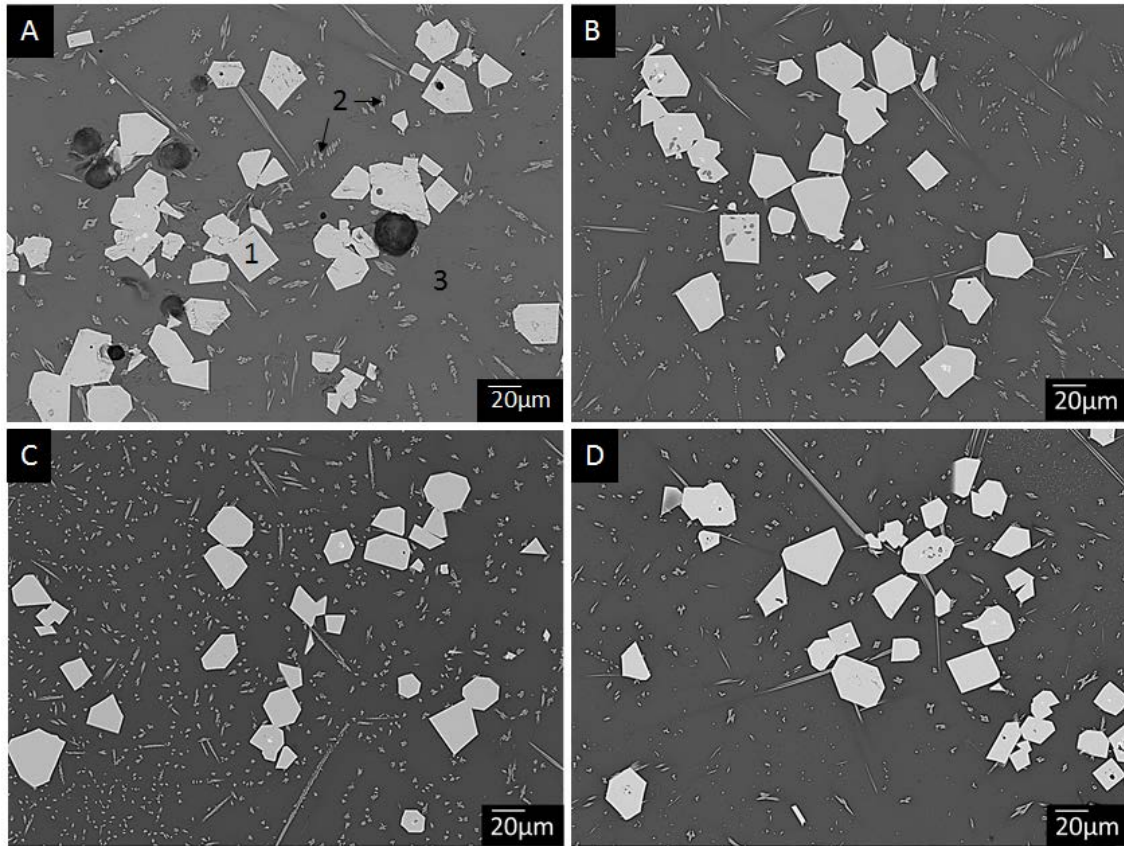

Fig. 1. SEM images comparing the microstructures of glass-ceramic samples A-D. Crystalline phases consist of two major phases zircon (1) and rutile (2) dispersed in a glass matrix (3).

Formulation Matrix

Figures 2 and 3 demonstrate the influence of the glass component on the crystalline phase assemblage achieved. Zirconolite formation is thermodynamically unfavourable compared to other crystalline phases; sphene ($CaTiSiO_5$), zircon ($ZrSiO_4$) and rutile (TiO_2).[4] XRD traces in Figure 2 demonstrate how the aluminium concentration in the glass phase significantly increases the yield of zirconolite thus reducing the presence of unwanted phases. The gradual increase in aluminium results in an increase in the thermodynamic activity of silica in the glass phase subsequently favouring zirconolite formation. By increasing the ceramic fraction of the wasteforms the same affect was observed such that a higher yield of zirconolite was attained. Figure 3 demonstrates the reduction of sphene, zircon and rutile when the ceramic fraction is increased from 50 wt% to 70 wt%.
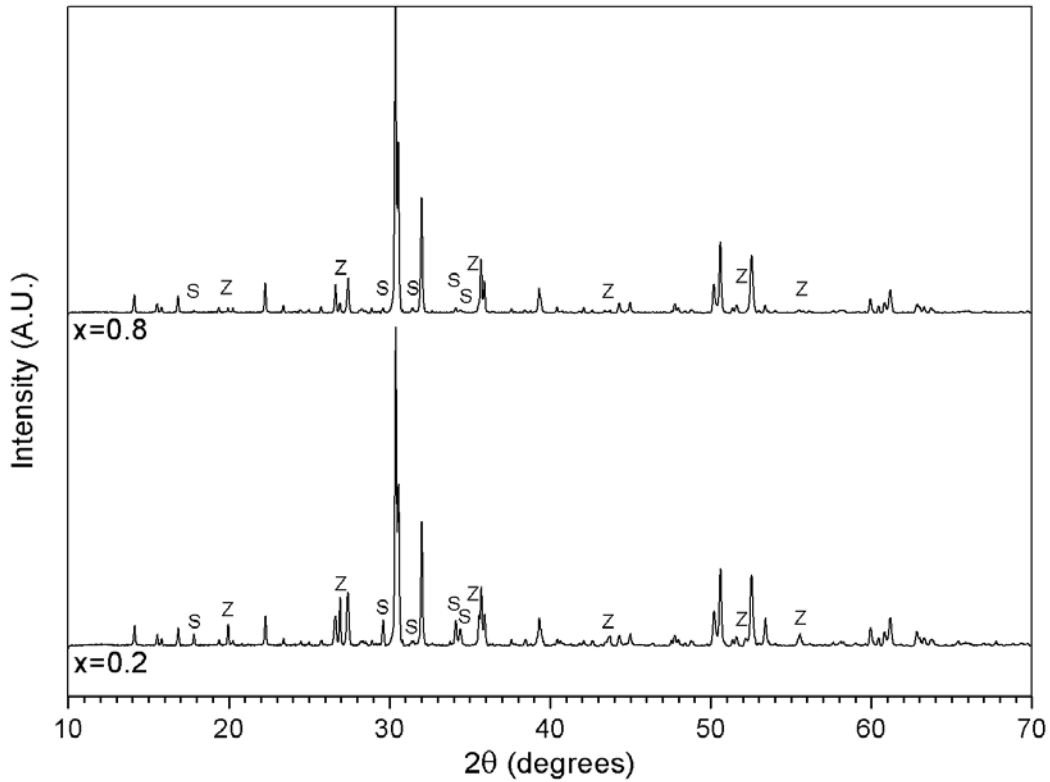
[1]Fig. 2. XRD plot showing a reduction in peak intensity of the unwanted phases sphene (pdf-card 01-085-0395) and zircon (pdf-card 04-007-5058) (labelled as S and Z, respectively) with an increase in Al concentration. All unlabeled peaks are correlated with the major phase zirconolite (pdf-card 04-007-6895).
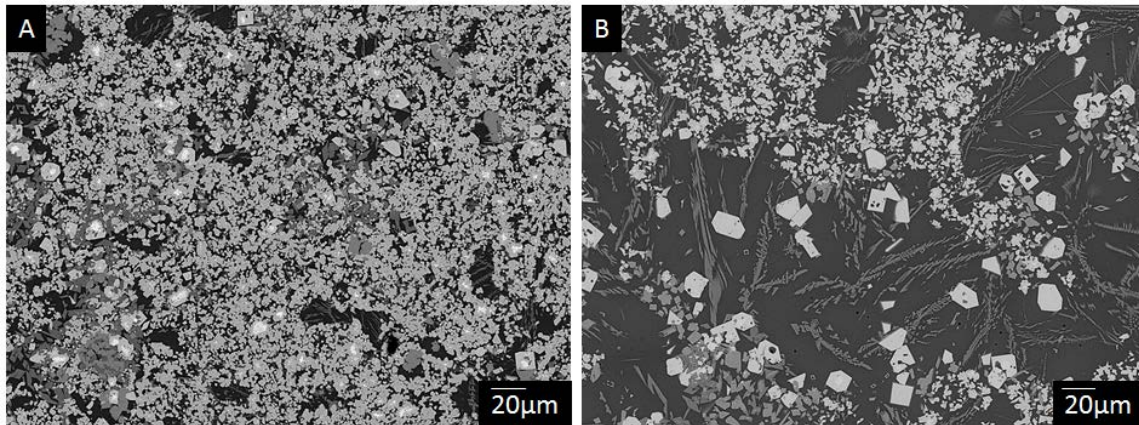

Fig. 3. SEM micrographs comparing the microstructures and phase assemblage of A) 70 wt% ceramic fraction and B) 50 wt% ceramic fraction. Both samples have the same glass composition $Na_2Al_{1.4}B_{0.6}Si_6O_{16}$.

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[1] Data shown for low glass fraction samples 30 wt% glass, 70 wt% ceramic with glass phase compositions $Na_2Al_{1.2}B_{0.8}Si_6O_{16}$ (Bottom) and $Na_2Al_{1.8}B_{0.2}Si_6O_{16}$ (Top).

CONCLUS ION

Zirconolite based glass-ceramic wasteforms are being developed by hot isostatic pressing for plutonium disposition. The importance of sample preparation has been demonstrated to attain high quality wasteforms and an optimized processing method has been achieved. The crystalline phase assemblage can be controlled as a function of the glass phase. Both the glass composition and fraction can have a significant effect on the final yield of zirconolite thus must be highly controlled.

ACKNOWLEDGEMENTS

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