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

Stephanie M. Thornber [a], Paul G. Heath [a], Gabriel P. Da Costa [a, b], Martin C. Stennett [a], Neil C. Hyatt [a, *]

[a] Immobilisation Science Laboratory, Department of Materials Science & Engineering, The University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK
[b] Department of Chemical Engineering & Petroleum Engineering, Universidade Federal Fluminense, Rua Passo da Patria 156, CEP 24210-240, Niteroi, RJ, Brazil

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
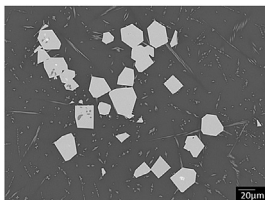
ABSTRACT

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.

* Corresponding author.
  E-mail address: n.c.hyatt@sheffield.ac.uk (N.C. Hyatt).

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

Table 2
Sample matrix and individual sample pre-treatments.

Sample	Pre-treatment	
	Ex-situ Calcination (°C)	In-canister Bake-out (°C)
A	−	300
B	−	600
C	600	300
D	600	−
E[a]	600	−

[a] Sample was fabricated from a glass frit precursor.

cold water to produce a granular frit material. The glass frit was crushed and sieved to <150 μm before milling with the ceramic forming oxides. This batch was calcined overnight at 600 °C to dry the ceramic forming oxides but did not have an in-canister bake-out prior to the HIP cycle.

All samples were HIPed at 1250 °C for 4 h under 103 MPa (15,000 psi) of pressure using argon gas as the pressure medium. The HIPed canisters were opened using a Buehler Abrasimet 250 saw or Buehler Isomet 1000 saw. Samples were polished and carbon coated for analysis using a Hitachi TM3030 analytical scanning electron microscope (SEM) with a 15 kV accelerating voltage and a working distance of 8 mm. Compositional analysis was conducted with a Bruker Quantax Energy Dispersive X-ray spectrometer system (EDX). Samples were ground and sieved for X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer with Cu Kα radiation (1.5418 Å); data were acquired between $10° \leq 2\theta \leq 70°$, with a step size of 0.02°, using a Lynxeye position sensitive detector. Thermogravimetric analysis (TGA) and mass spectroscopy (MS) were performed on the raw powders using a PerkinElmer STA 8000 TGA/DTA and a Hiden Mass Spectrometer. Samples were heated to 1250 °C at a heating rate of 10 °C/min in an argon and nitrogen atmosphere, respectively. Archimedes water displacement method was used to calculate the bulk density of the glass-ceramic wasteforms and HIP canister densifications. Helium gas pycnometry was used to determine the true density of the materials produced, each sample was run for 20 cycles under 12.5 psig of helium gas pressure.

3. Results

3.1. Raw materials

Powder X-ray diffraction (XRD) of the raw batch material before and after the overnight calcination was performed to characterise any significant changes to the raw reagents during either of the *ex-situ* calcination or in-canister bake-out high temperature pre-treatments. The XRD data in Fig. 1 revealed no major changes in the phases present and hence no evidence for gross decomposition of, or reaction between, the reagents up to 600 °C. However, minor changes were apparent with the appearance of a reflection attributed to cristobalite (SiO_2) at $2\theta = 23.73°$ (PDF card 04-008-7818) and the reduction of a minor sodium silicate (Na_2SiO_3) reflection at $2\theta = 29.36°$ (PDF card 00-016-0818).

Thermogravimetric analysis (TGA) (Fig. 2a) revealed a mass loss of 0.8 wt% from the milled precursor material between 250 °C and 700 °C (i.e. not subject to either *ex-situ* calcination or in-canister bake-out). This mass loss was not evident after *ex-situ* calcination of the precursor material at 600 °C for 16 h. Given the consistency of the XRD data in Fig. 1, the observed mass loss was not the result of a reaction or decomposition of reagents, and was inferred to be associated with adsorbed volatiles. Borax ($Na_2B_4O_7$) is commonly found as a decahydrate compound. Although it was batched in an anhydrous form in this study, it has the capacity to rehydrate. The borax decahydrate compound is reported to lose 8 molecules of bound water up to 142 °C, with the remaining 2 molecules retained up to 600 °C [11]. The dehydration behaviour of the milled batch material appeared consistent with that expected for the borax constituent. Further investigation of the borax reagent by TGA coupled with mass spectroscopy (MS) demonstrated the liberation of water (between ca. 60—800 °C) and carbon dioxide (between ca. 200—700 °C) corresponding to the mass loss observed in TGA analysis of the milled batch material, as shown in Fig. 2b. Consequently, we attribute the evolved gas from the milled batch material as being primarily associated with hydration and carbonation of the borax reagent, although we cannot rule out minor contributions from other reagents.

3.2. HIPed material

Back-Scattered Electron (BSE) micrographs revealed similar microstructures for samples A-D. No porosity was evident in high magnification BSE images of samples B-D (Fig. 3), whereas sample A had visible entrained porosity throughout. The entrained porosity within Sample A is a result of the low temperature 300 °C in-canister bake-out, which was insufficient to fully remove the adsorbed water and CO_2 inventory from the borax reagent, as shown by the TGA-MS data in Fig. 2. The glass-ceramic microstructures are otherwise consistent across all samples independent of the specific pre-treatment, as described below.

Further characterisation of the HIPed materials by SEM-EDX, Fig. 4, combined with XRD data, Fig. 5, established the major crystalline phase as zircon ($ZrSiO_4$), with minor rutile (TiO_2), and trace accessory phases of sphene ($CaTiSiO_5$), jadeite ($NaAlSi_2O_6$), quartz (SiO_2) and brookite (TiO_2) (PDF cards: 01-071-0991, 01-078-4188, 01-085-0395, 04-015-8184, 01-086-1630 and 00-015-0875, respectively). These ceramic phases were observed to be homogeneously distributed in the sodium aluminoborosilicate glass matrix. The phase assemblage is consistent with the previously investigated phase diagram, defined by glass:ceramic and Al_2O_3:B_2O_3 ratio, as described above and elsewhere [10]. Sodium has been reported to have a stabilising effect on brookite [12], which may explain the presence of this TiO_2 polymorph as a trace phase, crystallised from the glass matrix.

The density of the materials and compaction of canisters were determined using a combination of Archimedes water displacement and helium gas pycnometry. The low density of sample A in Table 3 corresponds to the entrained porosity and incomplete densification. Samples B − D have high relative densities, > 98% theoretical. Table 3 shows that the overnight calcination reduces the packing density of the batch in the HIP canister due to inconsistent agglomeration of the powder. This could be ameliorated by grinding the powder after the calcination; however, this would exacerbate the rehydration process by increasing the powder surface area. As a result, the powder was packed into the canisters immediately after the calcination to minimise the time from the furnace to canister evacuation, thus minimising the time available for the uptake of water (this period was kept to 60 ± 15 min when preparing each sample).

3.3. Use of a glass frit precursor

Sample E was fabricated by HIPing from a glass frit precursor of the same stoichiometric composition as the target glass phase in sample A-D ($Na_2Al_{0.5}B_{1.5}Si_6O_{16}$). The frit was batched with the ceramic forming reagents and milled under the same conditions as samples A-D. Due to the high content of refractory components SiO_2 and Al_2O_3 in the glass batch, the glass melt was highly viscous
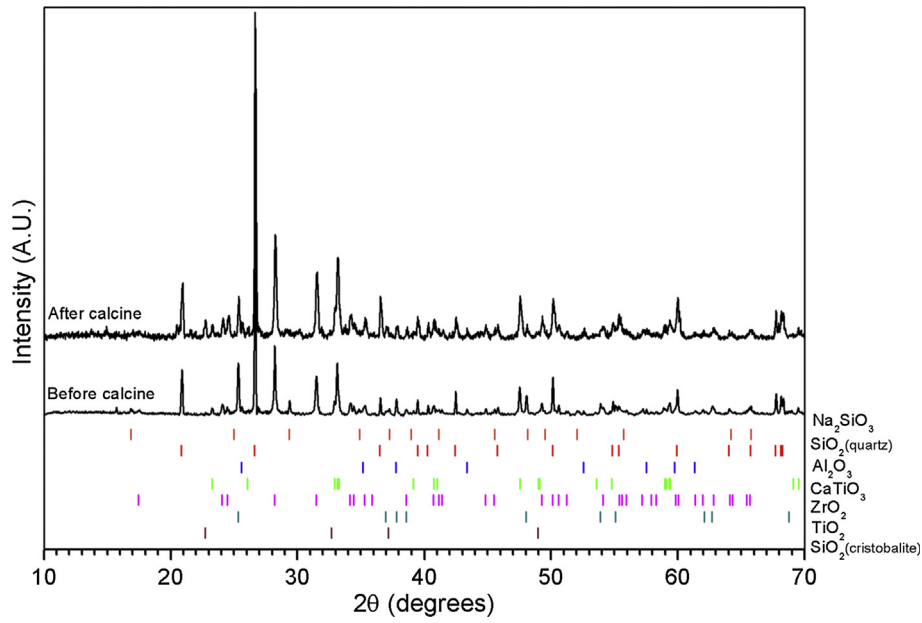
Fig. 1. XRD data for the raw batch constituents before and after *ex-situ* calcination at 600 °C for 16 h in air. The relative intensity of reflections associated with Na_2SiO_3 are reduced post-calcination and a new reflection at $2\theta = 23.73°$ relative to cristobalite is seen after calcination.
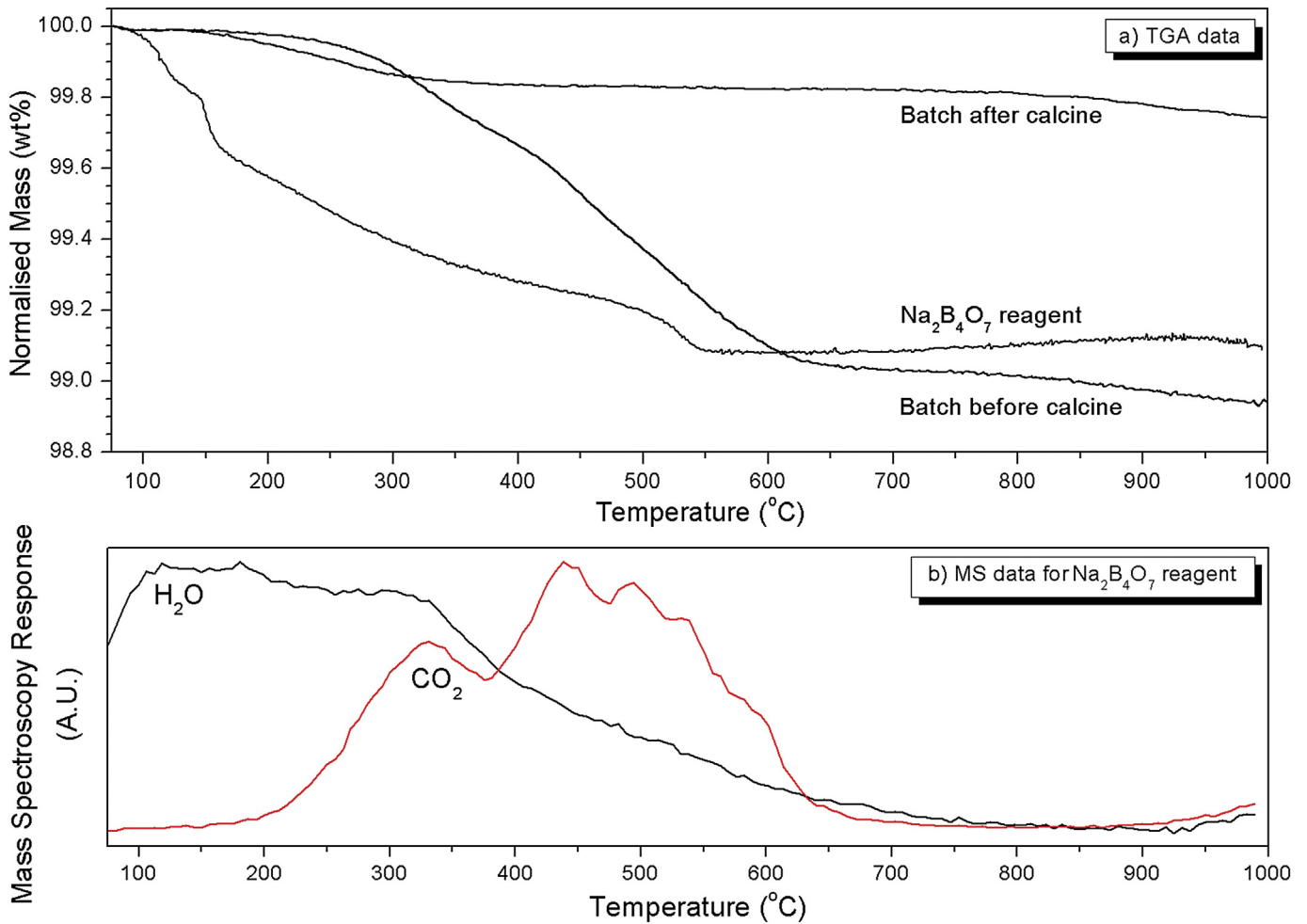

Fig. 2. a) TGA analysis of the borax $Na_2B_4O_7$ reagent and the raw batch constituents before and after *ex-situ* calcination at 600 °C showing a mass loss of 0.8 wt% between 250 and 700 °C, which is not apparent after *ex-situ* calcination. b) Mass Spectroscopy response for the borax reagent showing the evolution of H_2O and CO_2 over the mass range corresponding to the mass loss observed up to 700 °C in TGA data.
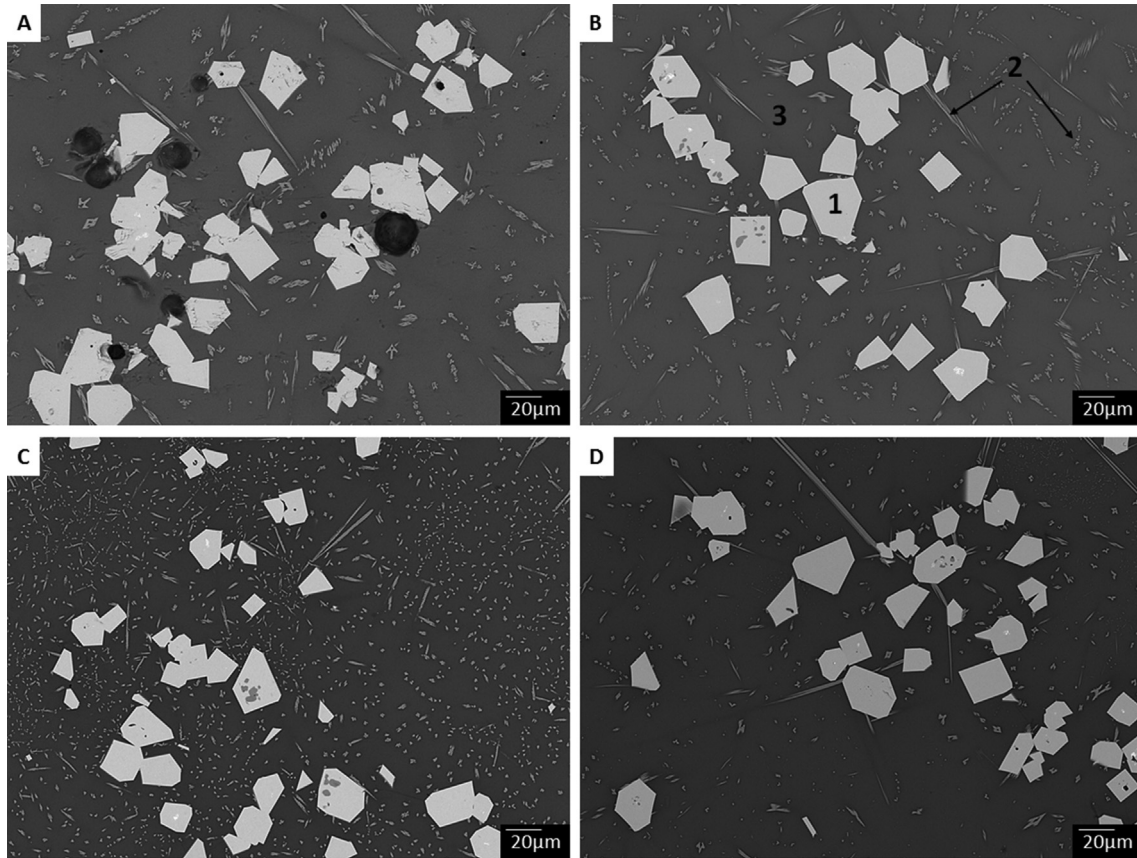
Fig. 3. BSE micrographs of samples A-D showing similar microstructures and phase assemblage independent of the pre-treatment applied, except for the presence of significant porosity in sample A. Major phases identified; 1) Zircon − $ZrSiO_4$, 2) Rutile − TiO_2 and 3) Amorphous glass phase.
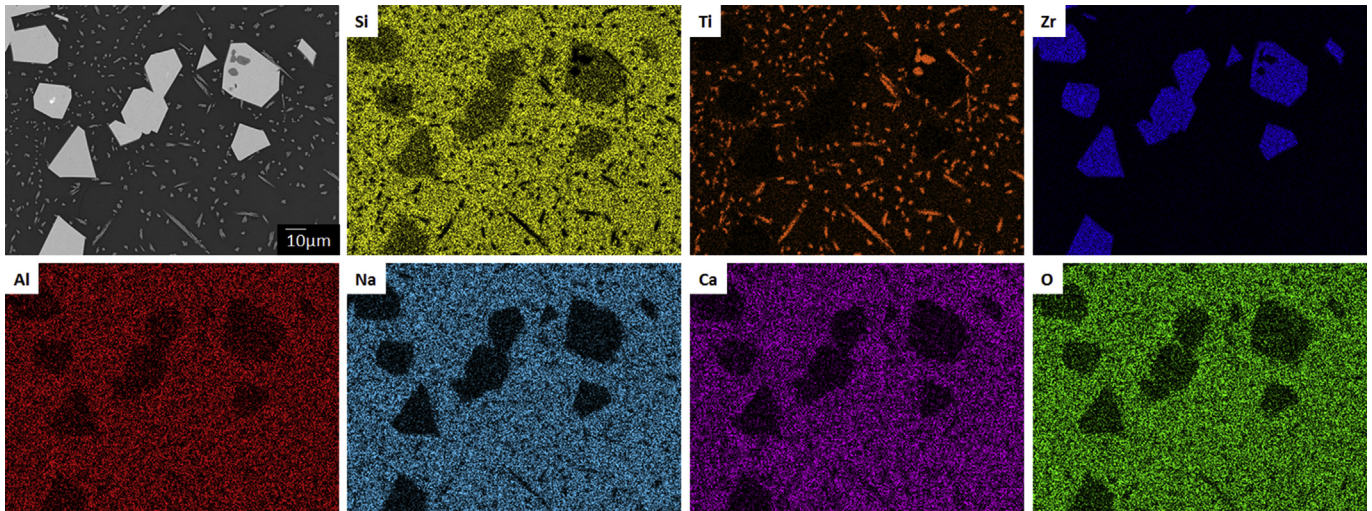

Fig. 4. EDX map for sample C (600 °C *ex-situ* calcination plus 300 °C in-canister bake-out) showing the distribution of elements between the major crystalline phases and glass matrix.

when poured at 1500 °C to form a frit. The glass was confirmed to be fully amorphous by XRD (data not shown). As for samples A-D, the HIPed wasteform fabricated from a glass frit comprised zircon as the major crystalline phase. The XRD plot in Fig. 6 compares XRD data for sample E against sample D that had the same pre-treatment (*ex-situ* calcination). Zircon ($ZrSiO_4$) is accompanied

with minor phases rutile (TiO_2) and sphene ($CaTiSiO_5$), and trace phases quartz (SiO_2), jadeite ($NaAlSi_2O_6$), baddeleyite (ZrO_2) and aluminium titanate (Al_2TiO_5) (PDF cards: (01-071-0991), (01-078-4188), (00-025-0177), (01-086-1630), (00-022-1338), (00-013-0307), (04-011-9497), respectively). As expected, zircon is present as large angular crystals and the minor phases are distributed in the
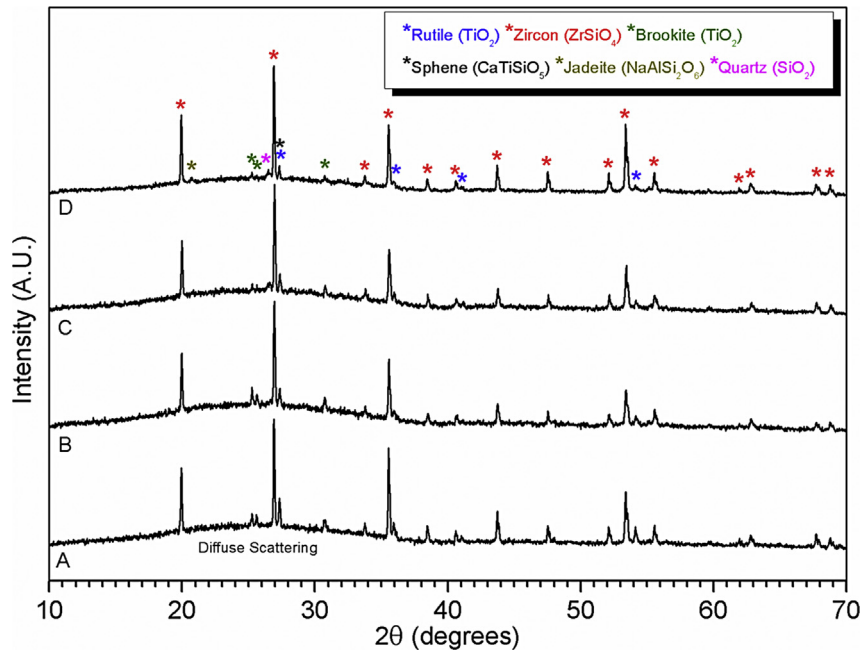
Fig. 5. XRD data for samples A-D (A − in-canister bake-out at 300 °C, B − in-canister bake-out at 600 °C, C − *ex-situ* calcination at 600 °C plus in-canister bake-out at 300 °C, D − *ex-situ* calcination at 600 °C). The phase assemblage is the same across all samples with only a small change in relative intensity of reflections associated with minor and trace phases.

Table 3
Summary table of material and canister densifications for samples A-D.

Sample	Total can evacuation time (mins) ($\pm$2.5)	Packing density (g/cm^3) ($\pm$0.04)	Pycnometry density (g/cm^3)	Monolith density (g/cm^3)	Material densification (%) ($\pm$2%)	Canister internal volume densification (%) ($\pm$2%)	Overall canister densification (%) ($\pm$2%)
A (300 °C in-canister bake-out)	960	1.66	2.7907 $\pm$ 0.002	2.7177 $\pm$ 0.025	97	31	22
B (600 °C in-canister bake-out)	480	1.57	2.744 $\pm$ 0.004	2.7758 $\pm$ 0.006	101	41	29
C (600 °C *ex-situ* calcination + 300 °C in-canister bake-out)	150	1.37	2.7792 $\pm$ 0.003	2.7584 $\pm$ 0.019	99	47	34
D (600 °C *ex-situ* calcination)	45	1.38	2.8287 $\pm$ 0.002	2.7802 $\pm$ 0.015	98	44	32
E (600 °C *ex-situ* calcination)	<190[a]	1.62	2.8428 $\pm$ 0.001	2.7880 $\pm$ 0.018	99	40	28

[a] The evacuation was interrupted, meaning the evacuation time could not be determined with precision.

glass matrix, shown in Fig. 7. Bright spots present at the centre of the zircon crystals were Zr rich and correspond with baddeleyite reflections present in the XRD data. The overall crystallite size is significantly smaller than those in the oxide samples, implying a reduced rate of crystal growth.

4. Discussion

It has been shown, at laboratory scale, that high temperature pre-treatment of the reagent batch, prior to the HIP cycle, is necessary for achieving high quality wasteform materials when using oxide precursors. The in-canister 300 °C bake-out was insufficient to remove the adsorbed water and CO_2 associated with the borax reagent as identified by the TGA-MS data. This resulted in the evolution of trapped volatiles during the HIP cycle, creating a porous wasteform product. The liberation of volatiles, pressurises residual porosity and provides an opposing force to sintering, thus inhibiting densification. In extreme cases the internal gas pressure may increase beyond that of the external isostatic pressure and overcome the deformation resistance of the canning material, resulting in porosity and canister expansion [13]. The level of

volatiles present in the non-heat treated powders was not enough to cause expansion of the canister, but did increase the amount of porosity present in the final wasteform. These consequences are undesirable: full densification of the wasteform was not achieved, the entrained porosity provides a pathway for water ingress and potentially increases the risk of radionuclide release during geological disposal, and irregular canister deformation puts additional stress on the welds, which could result in canister failure during processing. The *ex-situ* and in-canister high temperature (600 °C) pre-treatments both successfully removed the entrained volatile constituents, producing high quality, dense HIPed wasteforms. The final densities and densification factors for each canister are listed in Table 3, which highlights the lower density of sample A due to the entrained porosity.

The *ex-situ* and in-canister pre-treatments did not result in any significant reactions between precursors except for the loss of adsorbed water and CO_2. The final wasteform microstructure and phase assemblage were not significantly disrupted by the pre-treatment process, appearing consistent across all four samples. Zircon formed as the major phase in 10−30 μm crystallites distributed homogeneously throughout the glass matrix, with
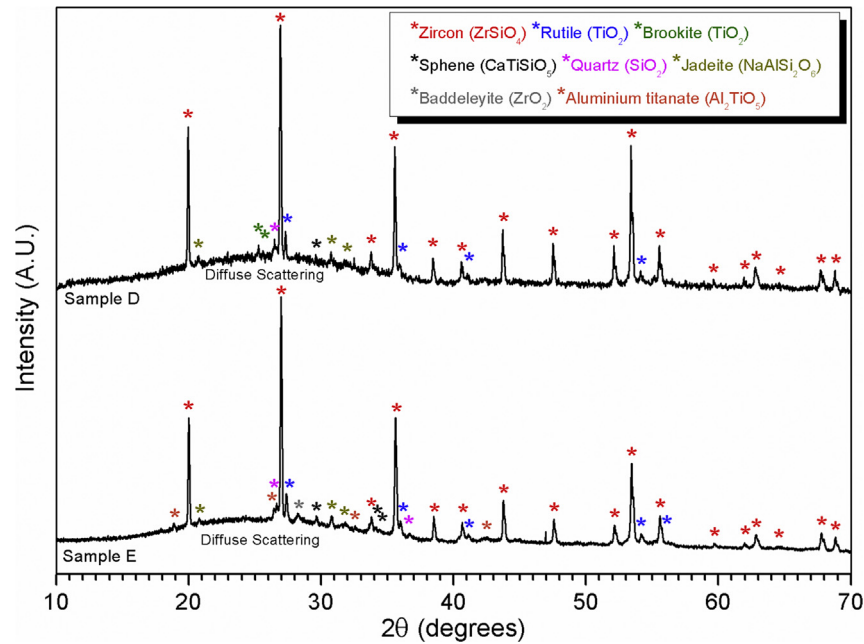
Fig. 6. Sample E XRD data compared against Sample D, which had the same pre-treatment (600 °C *ex-situ* calcination) showing similar crystalline phase assemblages.
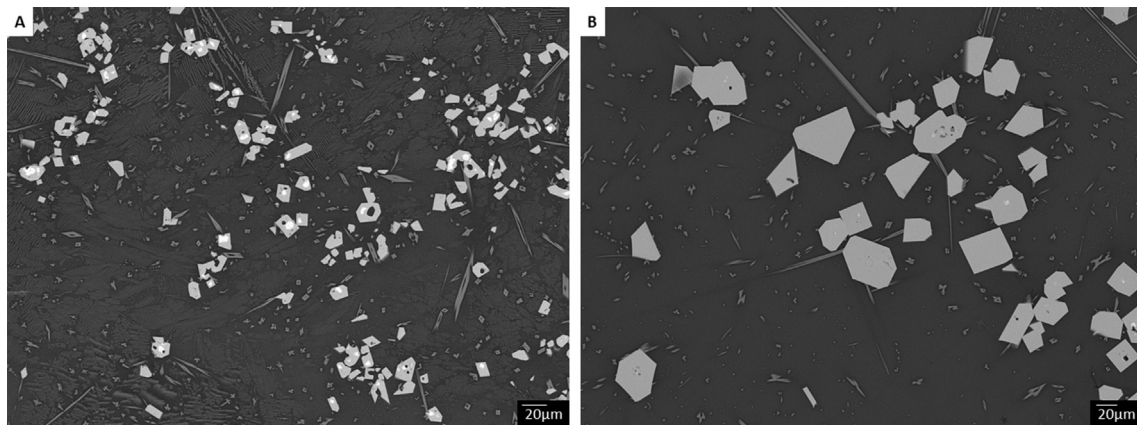

Fig. 7. SEM images comparing microstructure and crystal size for A) sample E − glass frit precursor and B) sample D − oxide precursors (both with 600 °C *ex-situ* calcination).

minor phase rutile (TiO_2) and additional trace phases; sphene ($CaTiSiO_5$), jadeite ($NaAlSi_2O_6$), quartz (SiO_2) and brookite (TiO_2). The Zr-rich spots present in sample E could imply the ZrO_2 particles act as nucleation sites for zircon formation. It is thought that the minor and trace phases present in the HIPed wasteforms recrystallized from the glass during the slow cooling step of the HIP cycle, but the zircon crystals formed at the processing temperature. This would explain the larger size of the zircon crystals, which had more time for crystal growth relative to the other crystalline phases. Further work is underway to identify the mechanisms controlling crystalline phase formation.

Small variations were observed in the fractions of trace phases, but this was within the normal variation expected between identical laboratory scale HIP samples, based on repeat experiments. This is encouraging with respect to optimising sample quality and reproducibility, as well as sample throughput. The *ex-situ* calcination afforded an equivalent product to the in-canister bake-out without detrimental effects to the microstructure, phase assemblage or densification. The option of utilising this *ex-situ* process to

improve sample throughput may now be considered.

The high temperature (600 °C) in-canister bake-out effectively evacuated the canister and removed volatiles to produce a dense wasteform. However, it required several hours to reach optimum vacuum pressure, even when using laboratory scale sample volumes (30 ml). Sample B (600 °C in-canister bake-out) took 8 h for complete evacuation before sealing. This could severely limit the throughput of waste packages on a full scale HIP plant or necessitate the use of multiple bake-out stations operating in parallel. The *ex-situ* calcination has been shown to produce a material of comparable quality and provided the most rapid canister evacuation - Sample D (600 °C *ex-situ* calcination only) was prepared after only 45 min evacuation.

There may also be an accompanying effect of increased gas permeability through the sample due to the lower packing density of the powders caused by agglomeration during the *ex-situ* calcination because of the high glass fraction. A lower packing density typically increases gas permeability [14], which, along with the prior removal of volatiles, also results in a faster canister evacuation

rate. The packing density of the batched powders is considered an important factor in the densification of the materials. Close packed particles aid the sintering process by improving heat transfer through the material, accelerating grain boundary growth and removing interconnected porosity [15,16]. Evacuation of the canister reduces the effective internal pore pressure during sintering that acts against densification by pushing grain boundaries apart. This reduction in pore pressure maximises the effect of the external isostatic pressure on the densification. Consequently, a high packing density is desirable when fabricating powder wasteforms, but because of the reduced gas permeability associated with a high packing density, optimisation of the evacuation and bake-out stages is important to maximise sample throughput and efficiency of the HIP plant line. It is also relevant to note that the powders were packed manually with an applied uniaxial pressure in the laboratory, however, this process will be different on an industrial scale HIP plant where vibratory packing will likely be utilised.

From the final canister densifications and material densities it can be concluded that the reduced packing density did not inhibit the compaction of the canister or final wasteform quality. Although the single *ex-situ* calcination at 600 °C provided the shortest evacuation time, it cannot be assumed prompt HIPing of the calcined batch will always be possible. Consequently, it was considered to couple the 600 °C *ex-situ* calcination with the 300 °C in-canister bake-out (sample C), as a suitable compromise between assuring sample quality and reproducibility, and enhancing wasteform throughput (2.5 h evacuation). This two-step procedure afforded a wasteform with no entrained porosity, uniform densification and a predictable phase assemblage and microstructure.

The HIP sample fabricated from a glass frit afforded a comparable microstructure and phase assemblage to the samples fabricated from oxide precursors, with zircon as the major crystalline phase. It was observed that the zircon crystallites were significantly smaller in size within the sample fabricated from a glass frit, compared to the crystallites within the samples fabricated from oxide precursors. One possible explanation for this observation is that crystal growth is limited when a glass frit is utilised due to slower diffusion rates before reaching full melt conditions. Slower diffusion rates may have inhibited the growth of the crystals, and may also explain the presence of ZrO_2 at the centre of the zircon crystals as a result of incomplete diffusion. However, further investigation is required to resolve this hypothesis.

Using a glass frit precursor is a potentially preferable method for batching the glass-ceramic wasteforms, to mitigate hydration and carbonation issues with the oxide precursor materials. The frit was formed by quenching the melt from 1500 °C. The melt was viscous but fully amorphous. Changes to the glass-ceramic formulation to attain the desired zirconolite based phase assemblage, could make the glass difficult to produce. A highly refractory glass would require high temperatures and high energy consumption to produce a homogeneous melt, and may also result in a glass too viscous to pour from the melter system. This could present problems or introduce limitations that can be avoided by using oxide precursors, which have been shown to achieve high quality glass-ceramic wasteforms when utilising high temperature pre-treatments. Further development will continue to use oxide precursors and implement the two step pre-treatment during sample preparation, comprising an *ex-situ* calcination at 600 °C followed by an in-canister bake-out at 300 °C.

5. Conclusions

Hot isostatic pressing is a proposed method to consolidate glass-ceramic wasteforms for immobilisation of plutonium residues. The preparation of HIP canisters was investigated to increase sample throughput and the efficiency of the HIP process. The limiting step was the bake-out during evacuation of the canisters, which is essential for producing high quality wasteforms. A high temperature in-canister bake-out achieved excellent material densification by removing all volatiles, including adsorbed water and carbon dioxide from the problematic anhydrous borax reagent. The overnight high temperature *ex-situ* calcination also produced a high quality material and reduced the required bake-out time by two thirds. As a compromise between sample throughput, quality and reproducibility, it was resolved to use the two step pre-treatment comprising a high temperature *ex-situ* calcination followed by a low temperature in-canister bake-out for future laboratory scale research. Using a glass frit is potentially a more straight forward way of adding the glass formers and achieved similar products to using oxide precursors, however the utility of this approach depends on the composition and refractory nature of the glass. Although zirconolite was not formed within the phase assemblage of the glass-ceramics studied here, the optimisation of pre-treatment parameters for removal of volatiles will be readily transferred to an optimised phase assemblage derived from the same precursor materials. Further work is underway to optimise the glass-ceramic formulation and obtain a high fraction zirconolite glass-ceramic wasteform utilising the two-step pre-treatment process, developed here, prior to canister sealing and subsequent HIP cycle.

References

[1] Nuclear Decommissioning Authority, Conditioning of Plutonium Residues by Hot Isostatic Pressing and Options for Packaging and Disposal (Pre-conceptual Stage) Summary of Assessment Report, 2009.
[2] Nuclear Decommissioning Authority, NDA: Plutonium Strategy - Current Position Paper, 2011.
[3] N.C. Hyatt, Plutonium management policy in the United Kingdom: the need for a dual track strategy, Energy Policy 101 (99) (2017) 303–309.
[4] C.R. Scales, E.R. Maddrell, N. Gawthorpe, B.D. Begg, S. Moricca, R.A. Day, Development of a Process for the Immobilisation of Actinide Containing Residues on the Sellafield Site, ICEM, Scotland, UK, 2005.
[5] R.A. Day, S. Moricca, M.W.A. Stewart, B.D. Begg, E.R. Maddrell, C.R. Scales, N. Gawthorpe, Technical Demonstration of Zirconolite Glass-ceramics Processed in a Hot Isostatic Press: an Option for Immobilisation of Actinide Containing Residues at Sellafield, ICEM, Scotland, UK, 2005.
[6] W.J. Weber, A. Navrotsky, S. Stefanovsky, E.R. Vance, E. Vernaz, Materials science of high-level nuclear waste immobilisation, MRS Bull. 34 (2009) 46–53.
[7] W.E. Lee, M.I. Ojovan, M.C. Stennett, N.C. Hyatt, Immobilisation of radioactive waste in glasses, glass composite materials and ceramics, Adv. Appl. Ceram. 105 (1) (2006) 3–12.
[8] E.R. Merz, C.E. Walter, Disposal of Weapon Plutonium, Kluwer Academic Publishers, Netherlands, 1996.

[9] D. Wahlquist, K. Bateman, T. Malewitz, in: Proceeding ASME 2014 Int. Mech. Congr. Expo., Remote Sealing of Canisters for Hot Isostatic Pressing, 2014.

[10] E. Maddrell, S. Thornber, N.C. Hyatt, The influence of glass composition on crystalline phase stability in glass-ceramic wasteforms, J. Nucl. Mater 456 (2014) 461—466, http://dx.doi.org/10.1016/j.jnucmat.2014.10.010.

[11] A. Ekmekyapar, A. Baysar, A. Kunkul, Dehydration kinetics of tincal and borax by thermal analysis, Ind. Eng. Chem. Res. 36 (1997) 3487—3490.

[12] A. Di Paola, M. Bellardita, L. Palmisano, Brookite, the least known TiO2 photocatalyst, Catalysts 3 (1) (2013) 36—73.

[13] D.S. Schwartz, D.S. Shih, R.J. Lederich, R.L. Martin, D.A. Deuser, Development and scale-up of the low density core process for Ti-64, in: Mater. Res. Soc. Symp. Proc., Materials Research Society, San Francisco USA, 1998, pp. 224—230.

[14] Y. Gu, X. Lui, G. Meng, D. Peng, Porous YSZ ceramics by water-based gel-casting, Ceram. Int. 25 (1999) 705—709.

[15] H.V. Atkinson, S. Davies, Fundamental aspects of hot isostatic pressing: an overview, Metall. Mat. Trans. 31A (2000) 2981—3000.

[16] M. Nanko, K. Ishizaki, T. Fujikawa, Porous ceramic filters produced by hot isostatic pressing, J. Am. Ceram. Soc. 77 (9) (1994) 2437—2442.