Article:
Thornber, S.M., Stennett, M.C., Vance, E.R. et al. (6 more authors) (2018) A preliminary validation study of PuO2 incorporation into zirconolite glass-ceramics. MRS Advances, 3 (20). pp. 1065-1071. ISSN 2059-8521

https://doi.org/10.1557/adv.2018.109

MRS Advances

A preliminary validation study of PuO_2 incorporation into zirconolite glass-ceramics.

Journal:	*MRS Advances*
Manuscript ID	MRSAdv-2017-0104
Manuscript Type:	Regular Article
Date Submitted by the Author:	12-Dec-2017

Complete List of Authors:	Thornber, Stephanie; The University of Sheffield, Materials Science and Engineering Stennett, Martin; University of Sheffield, Materials Science and Engineering Vance, Eric; Australian Nuclear Science and Technology Organisation, synrocANSTO Chavara, Dorji; Australian Nuclear Science and Technology Organisation, synrocANSTO Watson, Ian; Australian Nuclear Science and Technology Organisation, synrocANSTO Jovanovic, Miodrag; Australian Nuclear Science and Technology Organisation, synrocANSTO Davis, Joel; Australian Nuclear Science and Technology Organisation, synrocANSTO Gregg, Dan; Australian Nuclear Science and Technology Organisation, synrocANSTO Hyatt, Neil; University of Sheffield, Department of Engineering Materials

Keywords:	hot isostatic pressing (HIP), nuclear materials, Pu, waste management

A preliminary validation study of PuO_2 incorporation into zirconolite glass-ceramics.

Stephanie M. Thornber[1], Martin C. Stennett[1], Eric R. Vance[2], Dorji T. Chavara[2], Ian Watson[2], Miodrag Jovanovic[2], Joel Davis[2], Daniel Gregg[2] and Neil C. Hyatt[1]

[1]*Immobilisation Science Laboratory, Materials Science and Engineering Dept., The University of Sheffield, Mapping Street, Sheffield, S1 3JD, UK*
[2]*Australian Nuclear Science and Technology Organisation, Kirrawee DC, Locked Bag 2001, NSW 2232, Australia*

Abstract:

Zirconolite glass-ceramics are being developed as potential wasteforms for the disposition of Pu wastes in the UK. Previous studies utilised a variety of surrogates whilst this work uses both cold-press and sinter and hot isostatic press methods to validate the wasteform with PuO_2. A cold press and sinter sample was fabricated as part of a validation study for plutonium incorporation in hot isostatically pressed (HIPed) wasteforms. The results confirmed the cold-press and sinter, achieved successful waste incorporation and a microstructure and phase assemblage that was in agreement with those expected of a HIPed equivalent. A HIP sample was fabricated of the same composition and characterised by SEM and XRD. Results were in agreement with the sintered sample and achieved complete waste incorporation into the glass-ceramic wasteform. These samples have demonstrated successful incorporation of PuO_2 into glass-ceramic HIPed wasteforms proposed for processing Pu-based waste-streams in the UK.

Key Words: Zirconolite, glass-ceramic, plutonium, hot isostatic pressing (HIP)

Corresponding author: sthornber1@sheffield.ac.uk

Introduction

Hot isostatic pressing (HIPing) is a leading thermal treatment option for treating Pu-based wastes in the UK [1,2]. Pu-residues are a category of higher activity wastes requiring consolidation into long-term stable wasteforms. These wastes are highly variable in their physical form, from powders and sludges, to MOx fuel pellets and fuel pins [3]. They also fluctuate compositionally and have varying degrees of impurities present. As a result, a flexible process and wasteform matrix are required to accommodate the complexity and variability of these wastes in order to produce high quality wasteforms suitable for long-term storage and eventual geological disposal.

In addition to the Pu-residue wastes, the UK civil separated PuO_2 stockpile contains some material unsuitable for fuel fabrication and requires an immobilisation route [4]. In comparison to the complexity of Pu-residues, this material is relatively pure and has a fine particle size. It is envisaged that a consolidation route suitable for treating the Pu-residues inventory could also be applied to the fraction of PuO_2 stockpile material considered to be waste, or potentially, the whole stockpile in the future [5].

HIP has many benefits for processing these wastes including its wide operating window and process flexibility for handling different materials and waste feeds [6]. HIP is theoretically a batch process and processes waste hermetically sealed inside stainless steel canisters. Thus, no off-gases are produced during consolidation and minimal secondary wastes are produced throughout the plant line. This improves the safeguards and Pu accountancy ability in comparison to vitrification technologies that result in Pu contaminated secondary wastes, such as residues inside the melter.

Zirconolite glass-ceramics are considered potential wasteform matrices for processing these Pu-wastes. Zirconolite readily accommodates Pu into its structure and the glass phase accommodates waste impurities. In this regard, a zirconolite glass-ceramic with high glass content (~ 70 wt%) was previously demonstrated for the Pu-residue wastes [7]. More recent formulation work by Thornber *et al.* led to the current glass-ceramic formulation with its higher zirconolite content (70 wt%) being selected for Pu validation studies [8,9]. The present study looks at two samples, one HIP and one cold-press and sinter, to validate the waste incorporation behaviour with PuO_2 in this optimised glass-ceramic system. The sintered sample was first characterised to verify the reactivity of the PuO_2 waste before consolidating the larger scale HIP sample.

Experimental

Caution: Plutonium-239 is an alpha emitter (E_{max} = 5.16 MeV). All manipulations were performed in inert atmosphere gloveboxes and followed locally approved radioisotope handling guidelines and monitoring procedures.

The glass-ceramic formulation consisted of 30 wt% glass of target composition $Na_2Al_2Si_6O_{16}$. The ceramic phase was formulated for a stoichiometric substitution of Pu^{4+} on the Zr site, targeting $CaZr_{0.9}Pu_{0.1}Ti_2O_7$. The precursor materials were batched and milled at 500 rpm for 30 mins in a Retsch PM 100 planetary mill, before the PuO_2 was added. The PuO_2 was handled in an inert atmosphere glovebox. The PuO_2 was added to the dried precursor batch as a dry oxide powder and was mechanically stirred for homogenisation. The batch was calcined at 700 °C for 3 hr under a 3.5 % H_2/N_2 atmosphere. Once cool, Ni powder was added for controlled oxygen fugacity inside the HIP canister during processing. The powder was pressed into pellets and loaded into the 304 stainless steel HIP canister. The HIP canister was evacuated at room temperature and 300 °C before sealing, then HIPed at 1250 °C for 4 h under 100 MPa of argon gas pressure.

An additional pellet of 0.5 g was pressed and sintered at 1250 °C for 4 h in an air atmosphere. This cold-press and sinter sample provided verification of the PuO_2 reactivity in the glass-ceramic system before processing the larger scale HIP sample. The powder was taken from the same batch so it had undergone the same preparation process as the HIP sample.

Both the sintered sample and the HIP sample were analysed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to study the microstructures and phase assemblages of the glass-ceramic products. XRD was conducted on a Bruker D8 diffractometer with Cu Kα radiation (1.5418 Å), for 20 h between $10° \leq 2\theta \leq 80°$ with a 0.02° step size. The SEM analysis was performed on a Jeol 6300 microscope with a 15 kV accelerating voltage. Energy dispersive X-ray analysis (EDX) was performed using a Tracor Northern TN5502 EDX detector to gain information on the Pu partitioning between the crystalline and amorphous phases. All analysis was performed using monolithic samples, ground and polished flat, and carbon coated for SEM.

Results

The sintered sample allowed for validation of the PuO_2 reactivity before processing the larger scale HIP sample. The SEM image in figure 1 showed a microstructure similar to previous inactive HIP samples, with zirconolite crystals distributed throughout the glass matrix [9]. The XRD data, shown in figure 1, confirmed zirconolite as the major crystalline phase and $NiTiO_3$ as a minor phase (PDF cards: 04-007-6895 and 01-076-0336, respectively). The $NiTiO_3$ phase was a direct result of the oxidising atmosphere during sintering, which resulted in the oxidation of the Ni powder. This phase was found by SEM, to have a fine, dendritic microstructure, which precipitated out of the glass melt during cooling. This phase is labelled as **N** in the SEM micrograph in figure 1.

The XRD indicated the presence of two zirconolite polytypes. The monoclinic zirconolite-2M structure was the dominant polytype stabilised and was confirmed by the low angle peaks at 22.3°, 26.7° and 27.5° (PDF card: 04-007-6895). In addition, two low angle peaks at 15.8° and 28.8°, were indicative of the trigonal zirconolite-3T polytype (PDF card: 00-054-1132). Whilst there are minimal refined data available on the 3T structure, the presence of these low angle peaks indicated that both structures were present. This was in agreement with the literature, which reports a gradual transition of the 2M structure to the 3T structure with increased Pu substitutions [10].

SEM-EDX analysis of the sintered sample revealed smaller grains on the edge of the bulk zirconolite, with compositions indicative of zirconolite (**3T** in figure 1). It is possible these smaller grains are those of the trigonal 3T polytype, which resulted in the different morphology to the bulk zirconolite grains. The smaller size of these grains could imply this polytype formed later on in the HIP cycle, or even precipitated during cooling like the $NiTiO_3$ phase.

Most importantly, the SEM and XRD data did not reveal any traces of residual PuO_2 in the final glass-ceramic product. Full waste incorporation was achieved and SEM-EDX analysis confirmed the Pu had preferentially been incorporated into the target ceramic phase.

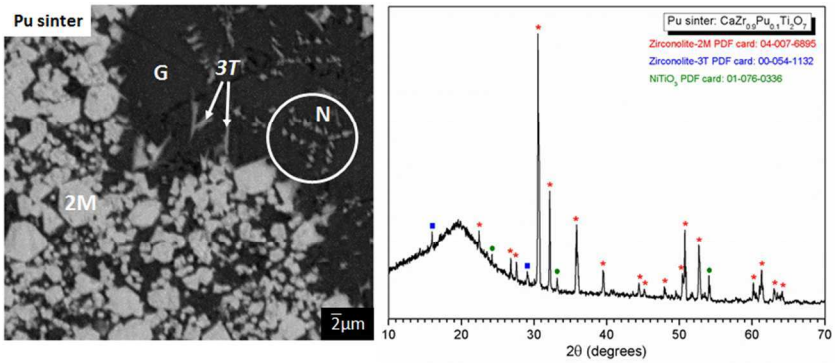

Figure 1: BSE micrograph and XRD pattern of the sintered glass-ceramic sample. Zirconolite was the major crystalline phase, with minor phase $NiTiO_3$, which was present due to the oxidising atmosphere during sintering. **2M** – zirconolite-2M, ***3T*** – zirconolite-3T and **N** – $NiTiO_3$ (PDF cards: 04-007-6895, 00-054-1132, 01-076-0336, respectively), **G** – glass phase. The large diffusive scattering in the XRD patterns was a result of the domed containment used during characterisation to avoid contamination of the X-ray diffractometer.

Whilst the sintered sample demonstrated evident porosity, the results confirmed excellent reactivity of the PuO_2 and successful waste incorporation into the glass-ceramic system. The HIPed sample of the same composition and same target stoichiometry provided further evidence for the successful disposition of Pu in these glass-ceramic wasteforms.

Figure 2 shows the HIP canister before and after consolidation, which achieved a volume reduction of ca. 62%. A sectioned sample was again characterised by SEM and XRD (figure 3). SEM confirmed a uniform microstructure of small zirconolite grains distributed throughout the glass matrix. No bright regions indicative of PuO_2 were observed, confirming complete incorporation of the waste. SEM-EDX again confirmed preferential incorporation of the Pu in the target ceramic phase.

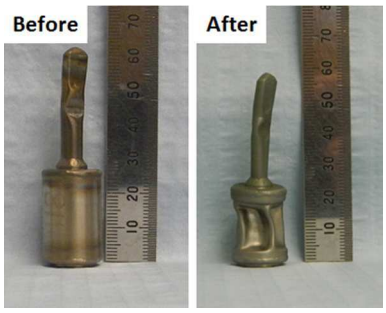

Figure 2: HIP canister before and after processing at 1250 °C, 4 h, under 100 MPa of pressure.

The XRD pattern in figure 3 shows the monoclinic zirconolite-2M structure was again stabilised as the primary ceramic phase. The two low angle zirconolite-3T reflections were present (15.8° and 28.8°) indicating a mix of the two polytypes, however, the 3T phase was not distinguished by SEM. The crystalline phase assemblage was in excellent agreement with the sintered sample, which proved to achieve a representative product of a HIPed equivalent. The absence of the $NiTiO_3$ phase in the HIPed sample was a result of

the reducing conditions during processing and confirmed this phase was a by-product of the oxidising atmosphere in the sintered sample.

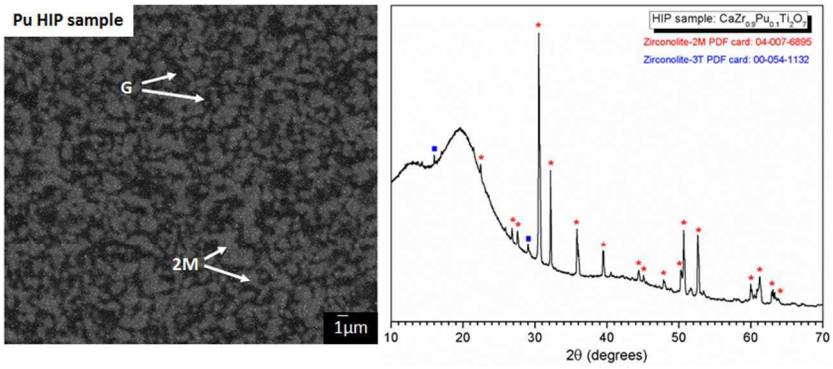

Figure 3: BSE micrograph and XRD pattern of the Pu HIP sample. Zirconolite was the only crystalline phase identified, distributed in the glass matrix. **2M** – zirconolite-2M (PDF card: 04-007-6895), **G** – glass phase. Zirconolite-3T was also identified in the XRD pattern but was not observed by SEM (PDF card: 00-054-1132). The large diffusive scattering in the XRD patterns was a result of the domed containment used during characterisation to avoid contamination of the X-ray diffractometer.

Discussion

A cold-pressed and sintered sample was compared against a HIPed sample as a validation study for PuO_2 waste incorporation into HIPed glass-ceramic wasteforms. The sintered sample was shown to be representative of the HIPed product and allowed for small scale verification to be done prior to the larger scale HIP sample.

For both samples discussed, complete waste incorporation was achieved and preferential partitioning of the Pu into the zirconolite phase was confirmed by SEM-EDX. XRD identified two zirconolite polytypes stabilised in both samples; zirconolite-2M and zirconolite-3T. Zirconolite is known to undergo structural transitions with increased lattice substitutions [11–14]. The results are in agreement with the literature, such that, at 0.1 f.u. substitution the zirconolite-2M structure was stabilised [10]. Begg *et* al. reported that the zirconolite-3T structure is increasingly stabilised with increased substitutions up to 0.3 f.u. when processed under reducing conditions [10]. Thus, the XRD results indicated the onset of this transition. It was interesting to note that the 3T polytype was stabilised in the sintered sample, processed under oxidising conditions. The 3T structure is reported to form under reducing conditions, under oxidising conditions the zirconolite-4M polytype is reported to form [10]. With progressively higher waste loadings and further substitutions, it would be expected that the 2M structure would transition to the 3T structure and finally a pyrochlore structure [10,12–14]

Previous studies typically use a sol-gel preparation route utilising colloidal solutions to achieve homogeneous mixtures [10,12,14]. However, for treating the PuO_2 stockpile and / or Pu-residues in the UK, a dry preparation route will most likely be used. As such, it was important to validate a realistic process using a dry oxide method. The results discussed here are in good agreement with previous studies, such that complete waste digestion was achieved with no detrimental effects to the microstructure or crystalline phase assemblage, and that preferential incorporation of Pu took place into the

zirconolite phase. This is very promising for further development of these wasteforms and the HIP technology, for processing the Pu-based wastes-streams into long-term wasteforms in the UK. We are currently investigating the effect of redox variations on the Pu valence state using diffuse reflectance spectroscopy.

Conclusions

Through the use of cold-press and sintered and hot isostatically pressed samples, a validation study for zirconolite glass-ceramic wasteforms for Pu disposition in the UK was performed. Results confirmed excellent PuO_2 incorporation into the zirconolite ceramic whilst maintaining a uniform microstructure and phase assemblage. The dry oxide processing route gave results that were comparatively in agreement with those from sol-gel processing routes, which was promising for further development of the HIP technology for treating Pu-based waste-streams in the UK.

Acknowledgements

This work was funded in part by the Nuclear Decommissioning Authority and the Australian Nuclear Science and Technology Organisation (ANSTO), in association with the EPSRC Decommissioning, immobilisation and storage solutions for nuclear waste inventories (DISTINCTIVE) - under grant EP/L014041/1. NCH is grateful to the Royal Academy of Engineering and the Nuclear Decommissioning Authority for funding. The authors are grateful to Mick Slater and Rick Short from NDA and Gerry Triani from ANSTO for helpful discussions.

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] C. R. Scales, E. R. Maddrell, J. Hobbs, R. Stephen, S. Moricca, M. W. A. Stewart, Building flexibility into the design of a pilot plant for the immobilisation of Pu containing residues and wastes., Brussels, Belgium, 2013.

[3] J.W. Hobbs, C.R. Scales, E.R. Maddrell, M.W.A. Stewart, S.A. Moricca, A programme to immobilise plutonium residues at Sellafield, in: Paper for the Institute of Nuclear Materials Management 53rd Annual Meeting, Orlando, Florida, 2012.

[4] N. C. Hyatt, Plutonium management policy in the United Kingdom: The need for a dual track strategy., Energy Policy. 101 (2017) 303–309.

[5] Nuclear Decommissioning Authority, Geological Disposal: Review of Alternative Radioactive Waste Management Options, 2017.

[6] 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, in: ICEM, Scotland, UK, 2005.

[7] 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, in: ICEM, Scotland, UK, 2005.

[8] S. Thornber, P. Heath, E. Maddrell, M.C. Stennett, N.C. Hyatt, Investigation of Processing Parameters for the Consolidation of Actinide Glass-Ceramic Wasteforms by Hot Isostatic Pressing, MRS Advances. (2017) 1–6. doi:10.1557/adv.2017.219.

[9] S.M. Thornber, M.C. Stennett, N.C. Hyatt, Investigation of Ce incorporation in zirconolite glass-ceramics for UK plutonium disposition, MRS Advances. (2017) 1–6. doi:10.1557/adv.2017.32.

[10] B.D. Begg, R.A. Day, A. Brownscombe, Structural Effect of Pu Substitutions on the Zr-Site in Zirconolite, MRS Proceedings. 663 (2000). doi:10.1557/PROC-663-259.

[11] M. Jafar, P. Sengupta, S.N. Achary, A.K. Tyagi, Phase Evolution and Microstructural Studies in $CaZrTi_2O_7$-$Nd_2Ti_2O_7$ System, Journal of the American Ceramic Society. 97 (2014) 609–616. doi:10.1111/jace.12664.

[12] C. Meng, X. Ding, W. Li, J. Zhao, H. Yang, Phase structure evolution and chemical durability studies of Ce-doped zirconolite–pyrochlore synroc for radioactive waste storage, Journal of Materials Science. 51 (2016) 5207–5215. doi:10.1007/s10853-016-9822-x.

[13] A. A. Coelho, R. W. Cheary, K. L. Smith, Analysis and Structural Determination of Nd-Substituted Zirconolite-4M, Journal of Solid State Chemistry. 129 (1997) 346–359.

[14] E. R. Vance, G. R. Lumpkin, M. L. Carter, D. J. Cassidy, C. J. Ball, R. A. Day, B. D. Begg, Incorporation of Uranium in Zirconolite, Journal of American Ceramics Society. 85 (2002) 1853–1859.