Journal of Nuclear Materials 454 (2014) 12–21

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Melt processed multiphase ceramic waste forms for nuclear waste immobilization

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HIGHLIGHTS

- We explored the feasibility of *melt processing* multiphase titanate-based ceramics.
- Melt processing produced phases obtained by alternative processing methods.
- Phases incorporated multiple lanthanides and transition metals.
- Processing in reducing atmosphere suppressed un-desirable Cs–Mo coupling.
- Cr partitions to and stabilizes the hollandite phase, which promotes Cs retention.

ARTICLE INFO

Article history:
Received 9 April 2014
Accepted 17 July 2014
Available online 24 July 2014

ABSTRACT

Ceramic waste forms are promising hosts for nuclear waste immobilization as they have the potential for increased durability and waste loading compared with conventional borosilicate glass waste forms. Ceramics are generally processed using hot pressing, spark plasma sintering, and conventional solid-state reaction, however such methods can be prohibitively expensive or impractical at production scales. Recently, melt processing has been investigated as an alternative to solid-state sintering methods. Given that melter technology is currently in use for High Level Waste (HLW) vitrification in several countries, the technology readiness of melt processing appears to be advantageous over sintering methods. This work reports the development of candidate multi-phase ceramic compositions processed from a melt. Cr additions, developed to promote the formation and stability of a Cs containing hollandite phase were successfully incorporated into melt processed multi-phase ceramics. Control of the reduction–oxidation (Redox) conditions suppressed undesirable Cs–Mo containing phases, and additions of Al and Fe reduced the melting temperature.

1. Introduction

Waste treatment technologies are an integral component to The United States Department of Energy (DOE) Fuel Cycle Research and Development (FCR&D) program. Successful waste treatment and storage are necessary to support next-generation nuclear energy development. A single waste form that can host all the waste elements in the projected aqueous reprocessing High-Level Waste (HLW) is most desirable [1].

The traditional method for HLW immobilization is to form borosilicate glass by a vitrification process, a practice currently used for defense and commercial waste [2]. Durable ceramic waste forms that incorporate a wide range of radionuclides have the potential to broaden the available disposal options and to lower the storage and disposal costs associated with advanced fuel cycles. Ceramic waste forms are tailored (engineered) to incorporate waste components as part of their crystal structure based on knowledge from naturally found minerals containing radioactive and non-radioactive species similar to the radionuclides of concern in wastes from fuel reprocessing. The ability to tailor ceramics to mimic naturally occurring crystals substantiates the long term stability of such crystals (ceramics) over geologic timescales of interest for nuclear waste immobilization [3].

Multiphase ceramics targeting an assemblage of titanate-based phases have been successfully demonstrated to incorporate

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http://dx.doi.org/10.1016/j.jnucmat.2014.07.035

various radioactive waste elements into a number of crystalline phases. Most notable are the synthetic rock (SYNROC) family of minerals developed in the 1980s that have been primarily produced by hot-pressing [4,5]. Melt processing of waste forms is considered advantageous over the conventional solid-state synthesis methods given that melters are currently in use for HLW vitrification in several countries, greatly facilitating the technology readiness of ceramic waste forms, and melter technology can reduce the potential for airborne contamination during pretreatment as compared to processes involving extensive powder handling operations.

There have been several comparative studies of crystalline ceramic waste forms produced by hot pressing and inductive melting [6,7]. These prior studies have indicated that the specimens fabricated by melt processing and solid state sintering exhibited similar mineral compositions, with the exception of a water-soluble molybdate phase observed in melt processing Mo containing waste streams in air. Under oxidizing processing conditions, attempts to make single phase hollandite (the host phase for Cs) ceramics are difficult and more often results in secondary metastable Cs containing phases [8]. It has been demonstrated that these secondary phases can be suppressed by controlling the starting compositions and the Ti^{3+}/Ti^{4+} during processing. Metal powder (Ti) additions to the batch material or hot pressing in graphite have been shown to be effective methods for controlling the redox conditions during sintering [9,10].

A major objective of the present work was aimed at varying the composition and processing conditions in order to mitigate Cs–Mo molybdate phase formation. In addition, there was particular interest regarding the characteristics of phase formation and elemental partitioning in melt processed ceramic composites. The intent of this work is to demonstrate the feasibility of melt processing technology to produce multiphase waste forms with phase composition comparable to conventional methods.

2. Composition development

2.1. Projected waste composition

The waste composition that formed the basis for the development and testing is given in Table 1. Noble metals, minor actinides and Tc were removed for cost and handling reasons. The MoO_3 targeted in this work was based on one possible reprocessing flowsheet, but other variants exist and more will be developed based in part on waste form studies such as this. Because this work incorporated varying Redox conditions and previous results indicated large concentrations of MoO_3 inhibited desired phase formation under oxidizing conditions, the MoO_3 concentration was targeted at 3 wt.% to simplify comparison among samples.

Table 1
Projected and re-normalized waste composition targeted in this study.

Group	Fuel[a]	SRNL[b]	Fuel[c]
Alkali	7.6	13.4	9.6
Alkaline Earth	8.3	12.9	10.6
Lanthanides	33.1	51.8	42.0
Actinides	4.0	–	–
Noble Metals	14.6	–	–
MoO_3	13.7	3.4	17.4
ZrO_2	13.7	12.1	17.4
TcO_2	2.7	–	–
Others	2.4	6.3	3.0
Total	100	100	100

[a] Projection.
[b] Does not include corrosion and process products.
[c] Renormalized to exclude corrosion and process products.

2.2. Single phase hollandite

Hollandite-type structures are a promising crystalline host for Cs, one of the more problematic fission products to immobilize. Melt processed single phase Cs-containing hollandite ceramics with Cr additions of the form $Ba_{1.0}Cs_{0.3}A_{2.3}Ti_{5.7}O_{16}$ (A = Cr, Fe, Al) were developed precursory to this work. Durability studies indicated that Cr additions increased Cs retention and suppressed secondary phase formation compared to Fe-hollandite analogs. Processing in various redox conditions affected the phase purity of Fe-containing hollandites whereas had negligible effect on the resulting phase purity in the Cr-containing hollandites. X-ray absorption spectroscopy confirmed the relative stability of Cr^{3+} as compared to Fe^{3+} in various redox conditions. It is speculated that Cr helps to stabilize the hollandite phase during forming which in turn promotes Cs incorporation into the hollandite [9]. Hollandite compositions with Cr additions are considered a promising phase for Cs-immobilization and served as the basis for multiphase ceramic waste form compositions presented in this work.

2.3. Calculation of multi phase waste form compositions

In this work, optimized single phase hollandite compositions based on Cr and Cr/Al/Fe additions were incorporated into multiphase ceramics targeting hollandite, perovskite/pyrochlore and zirconolite phase assemblages. The phase assemblages were designed based on combinations of the waste and additives (the primary additive being TiO_2) to target the desired phases (i.e. hollandite, perovskite/pyrochlore and zirconolite) upon melting. Literature data and valence state were used to predict which phases each element would partition to. Specifically, elements with a +3 or +2 valance with titania form pyrochlore and perovskite type structures resulting in $(A^{+2})TiO_3$ and $(A^{3+})_2Ti_2O_7$ type phases [11,12]. Zirconium has been demonstrated to partition to a $CaZrTi_2O_7$ zirconolite phase [13]. The Cs and Rb elements are known to partition to a hollandite structure based on the general formula $Ba_xCs_yM_zTi^{4+}_{8-z}O_{16}$ where M = metal cation and $z = 2x + y$ for trivalent cations and $z = x + y/2$ for divalent cations for charge compensation [8,14,15].

The waste and additive calculations were based on combining oxide and carbonate powders, as described in Section 3.1.1. Table 2 summarizes the two multiphase compositions (based on Cr and Cr/Al/Fe additions) that were prepared for this work, each with ~25 weight% waste loading and varying additive concentrations. Cr-MP denotes a multiphase assemblage targeting the Cr-hollandite analog and CAF-MP denotes a multiphase assemblage targeting the Cr/Al/Fe-hollandite analog. The batch oxide components in wt.% percent and associated target phase are listed in Table 3 for both multiphase compositions.

Table 2
Additive and waste concentrations (wt.%) used in this study.

Component	Target phase	CAF-MP	Cr-MP
Waste	Various	24.66	24.58
Al_2O_3	Hollandite	1.27	0
TiO_2	Various	49.16	49.01
CaO	Zirconolite	1.39	1.38
BaO	Hollandite	10.56	10.52
Fe_2O_3	Hollandite	6.65	0
Cr_2O_3	Hollandite	6.33	14.5