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Short communication

Composite wasteform based on SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) parent glass with zircon as the second component

M. Malek [a], M.R. Khani [a], P. Alizadeh [a,*], H. Kazemian [b,1]

[a] School of Engineering, Tarbiat Modares University, Tehran, Iran
[b] Nuclear Science and Technology Research Institute (NSTRI), P.O. 11365-3486, Tehran, Iran

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Abstract

Many different types of glass and ceramic wasteforms have been investigated for nuclear waste immobilization. This study deals with synthesizing composite wasteforms based on a parent glass belonging to the SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) system with the use of zircon as a second component. The fabrication involves powder mixing, pressing and pressureless sintering. The processing conditions were investigated so as to achieve the highest density and the best sintering temperature for different amounts of zircon, i.e. 5, 10 and 15 wt%. The sintered products were studied by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM); as well as ICP-MAS for leaching experiments. The most promising composite containing zirkelite and titanite crystals in a lead-rich glassy matrix was obtained at 700 °C for 10 wt% zircon.

Keywords: A. Sintering; B. Composites; C. Chemical properties; E. Nuclear application

1. Introduction

Many different types of glass and ceramic wasteforms have been investigated for nuclear waste immobilization [1]. The partial devitrification of the glass over time is the potential problem of vitreous wasteforms [2]. There has been much interest in using titanates with fluorite and fluorite-related structures, such as pyrochlore and zirconolite, as the most promising phases for actinide immobilization [3,4]. Zirconolite (nominally $CaZrTi_2O_7$) is the major phase of Synroc, a multiphase titanate ceramic, designed for the immobilization of high-level radioactive wastes [5].

It has been proposed that Synroc could be combined with a glassy phase to form a composite wasteform [6]. A ceramic–glass composite wasteform has been developed in which the crystalline phase is an aluminosilicate zeolite that is then combined with 25% glass frit and hot isostatically pressed [7]. A novel composite has been also reported that is made of a lead-containing glass matrix, into which particles of lanthanum zirconate pyrochlore are embedded in 10 and 30 vol% concentrations [8].

The present study takes advantage of a previous study on synthesizing a new glass–ceramic composition within the SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) system [9]. The most interesting aspect of the work is the addition of PbO to the main SiO_2–CaO–ZrO_2–TiO_2 system. This addition could reduce the liquidus temperature, facilitate the melting process and lower the crystallization temperature. The objective of this study is to consider forming a titanate composite based on the mentioned system, using zircon (proposed as an actinide wasteform itself, e.g. [3,10]) as the second component.

2. Experimental

The materials used in the present study were reagent-grade PbO, SiO_2, B_2O_3, K_2CO_3, $CaCO_3$, ZrO_2, and TiO_2; as well as zircon (Johnson Matthey). A parent glass was prepared in accordance with the following procedure. A lead frit primarily prepared by melting the following mixture at 900 °C for 2 h: PbO (63), SiO_2 (27), B_2O_3 (7.5), and K_2CO_3 (3.67) [i.e. K_2O

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[*] Corresponding author at: School of Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran. Tel.: +98 21 8288 4399.
E-mail address: p-alizadeh@modares.ac.ir (P. Alizadeh).

[1] Current address: R&D Lab, SPAG Co., Science & Technology Park of Tehran University, 1439814448, Tehran, Iran.

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(2.5)] (in wt%). The parent glass was, then, prepared by melting and quenching the following mixture at 1460 °C for 2 h: ZrO_2 (14.54), TiO_2 (18.85), $CaCO_3$ (11.81) [i.e. CaO (6.62)], and the lead frit (60) (in wt%). The product was ground and sieved at 45 μm (325 mesh). Three powder batches were wet-mixed with various amounts of zircon, actually 5, 10, and 15 wt%. The powder mixtures were pressed in a stainless steel die at a constant pressure of 70 MPa. The pressed pellets were finally heat-treated at different temperatures in the range 650–800 °C for 4 h, using heating rate of 20 °C min^{-1} in order to obtain the high-density samples.

The density (via Archimedes' method) and the shrinkage of each sample were determined with the aim of determining sintering temperature. The sintered products were, then, characterized by X-ray powder diffraction (XRD) using a Philips Xprt (Cu Kα radiation, 30 mA, 40 kV); and scanning electron microscopy (SEM) using a Philips XLΦ microscope. The micro-hardness of the products was also evaluated using a Bühler Micromet-1 tester, applying a load of 1000 g for 30 s (ASTM C730-98).

The leachability of the powdered samples can be measured by MCC-3 solubility test, in which samples of known surface area are immersed in the leachant for defined periods of time, using a fixed ratio of leachant volume to sample mass at temperatures in the range 40–190 °C [1,11]. In our experiment each sample was ground to pass through a 325-mesh screen and allowed to react with a volume of distilled water equal to ten times the sample mass, at a test temperature of 90 °C for periods of 1, 3, 5, and 7 days [11]. The concentration of the released species was measured with the use of ICP-MAS (Varian Liberty 150AX Turbo).

3. Results and discussion

The sintering temperatures leading to the highest density composites were determined to be 750, 700, and 700 °C for the samples with 5, 10, and 15 wt% zircon, respectively; with relative densities of 94, 93, and 81%. The XRD pattern of the sintered samples with different amounts of zircon is shown in Fig. 1, as well as that of the glass–ceramic at 780 °C. It should be mentioned that 10 wt% of silicon powder was added to each sample as an internal standard for peak positioning. It is clear from this figure that the composite samples contain the same phases, interestingly titanite and zirkelite. The latter is the different crystal structures of the composition $CaZrTi_2O_7$, and frequent intergrowths with zirkelite and zirconolite have been observed [4]. Fig. 2 shows SEM images of the composites with different amounts of zircon at sintering temperature. As seen in Fig. 2a–c, zirkelite particles are embedded in the same lead-rich glassy matrices revealed from EDX analyses. There is some expected residual porosity in the matrices, considering the relative densities, suggesting that sintering densification can be more developed. Although the relative densities decreased with the increase of zircon content, it should be noted that the rise of temperature in each case could result in bloating of the specimens. No major development of sintering defects, such as crack-like voids, was observed in the sintered samples,

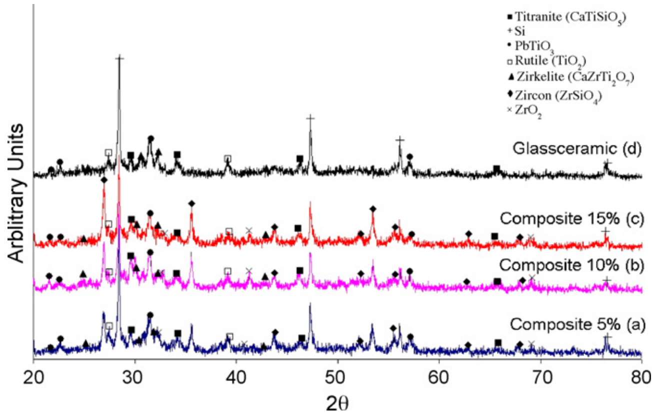

Fig. 1. XRD pattern of a composite containing: (a) 5 wt% zircon, sintered at 750 °C; (b) 10 wt% zircon, sintered at 700 °C; (c) 15 wt% zircon, sintered at 700 °C and as well as that of the glass–ceramic, heat-treated at 780 °C (d).

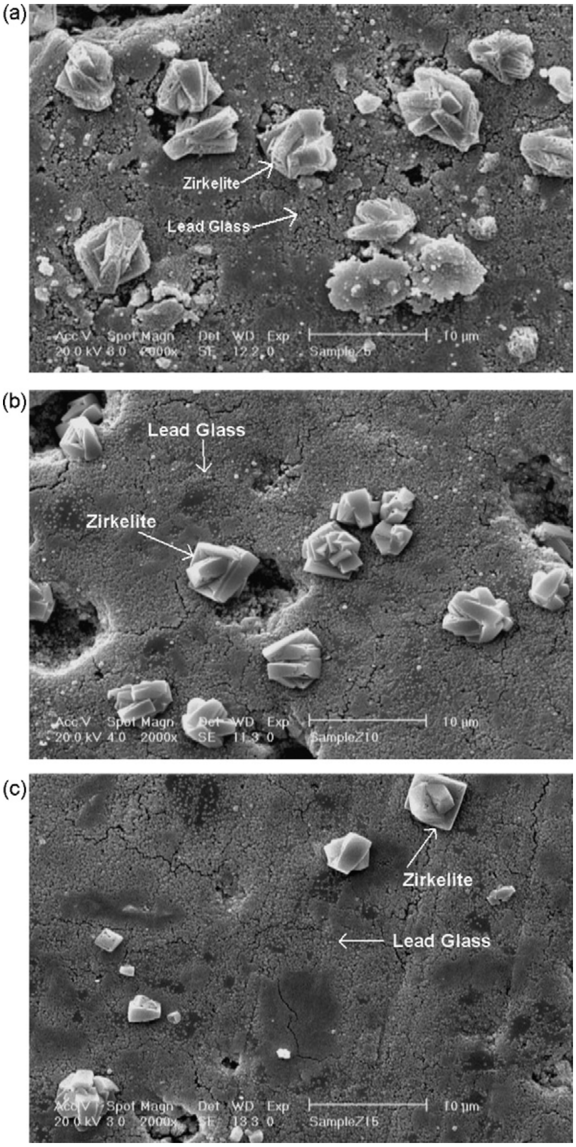

Fig. 2. SEM micrographs of the sintered composites with zircon amounts of 5 wt% (a), 10 wt% (b) and 15 wt% (c).

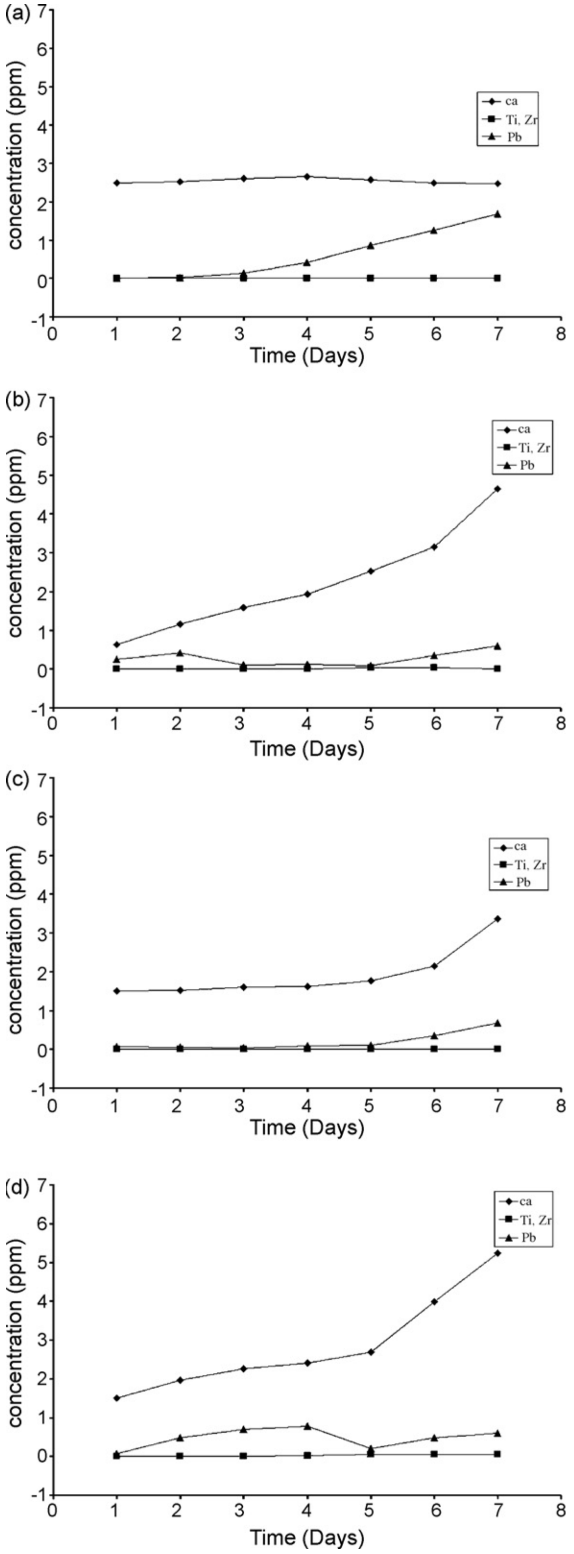

Fig. 3. The leaching rate of heat-treated glass–ceramic (a); and sintered composites with zircon amounts of 5 wt% (b), 10 wt% (c) and 15 wt% (d).

suggesting the relatively good mechanical strength and structural integrity of the composites. The Vickers micro-harness of the composite products was measured to be 2.2, 2.6, and 3.6 GPa for samples with 5, 10, and 15 wt% zircon, respectively. The rise of micro-hardness with the increase of zircon content is reasonably observed.

The result of leaching experiments is indicated in Fig. 3, showing the leaching rate (concentration of the released species Ca, Zr, Ti, and Pb versus time) of the heat-treated glass–ceramic and the sintered composites with different amounts of zircon. As seen in Fig. 3a for the glass–ceramic, Ti, Zr, and Ca species from crystalline phases have been negligibly released in the leachant within even 7 days, while Pb mainly from the lead-rich glassy matrix on the contrary shows an increased amount of dissolution. The release of ions from the glass–ceramic mostly depends on relative portioning between crystalline and glassy phase and on the dissolution behavior of these phases. As shown in Fig. 3b–d for the composites containing 5, 10, and 15 wt% zircon, respectively; extremely low solubility of Ti, Zr is reasonably observed (e.g. [1]); while observing the rise of Ca release specially from 5 days on, in all cases. Considering the chemical resistance, the composite with 10 wt% zircon seems to be the most promising one. However, it seems that the leaching rate is controlled by the most leachable elements (alkaline species) and may be limited by the leachability of the lead-containing glassy matrix.

4. Conclusions

Composite wasteforms based on a parent glass belonging to the SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) system with different amounts of zircon as a second component were fabricated and characterized, interestingly containing zirkelite and titanite crystals in a lead-rich glassy matrix. The fabrication involved powder processing and sintering at relatively low temperatures (<750 °C). No major development of sintering defects was observed in the samples. The leach resistance of the composites was mainly limited by the alkaline content and the leachability of the lead-containing glassy matrix. From the point of chemical resistance, composite sample with 10 wt% zircon seems to be the most promising one.

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