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Encapsulated gadolinium zirconate pyrochlore particles in soda borosilicate glass as novel radioactive waste form

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Abstract

Gadolinium zirconate pyrochlore crystals, with a potential for hosting radioactive elements, were encapsulated in a soda borosilicate glass matrix forming a composite material. The fabrication process involved mixing as a powder followed by hot pressing at a relatively low temperature of 620 °C. Composites containing pyrochlore particles of mean particle size <60 μm in concentration of up to 40 vol% exhibited a homogeneous distribution of the particles in the glass matrix. The absence of debonding of Gd zirconate particles or deflection of cracks during fracture, indicates that a strong interface between the glass matrix and the gadolinium zirconate particles was achieved, which suggests a high mechanical strength and hardness of the composites. Mechanical tests were carried out and it was confirmed that the presence of the gadolinium zirconate particles increased the Young's modulus and fracture toughness of the composite by 35% and $>100\%$, respectively, in comparison with plain borosilicate glass. The results indicate that the new waste forms are superior in terms of structural integrity and fracture behaviour than plain borosilicate glass waste forms.

Keywords: A. Hot pressing; C. Mechanical properties; D. Glass; E. Nuclear applications

1. Introduction

The immobilization of high-level nuclear waste (HLW) in borosilicate glasses has been developed to the industrial scale, and it can be considered as a well-established technology [1,2]. These glasses readily dissolve a wide range of radioactive waste compositions and they exhibit good glass-forming ability, chemical durability, mechanical integrity, and excellent thermal and radiation stability [1–3].

Encapsulation is an alternative approach to nuclear waste treatment, which relies on immobilizing radionuclides by isolating them from the environment within a protecting, chemical resistant matrix, rather then by dissolving them directly into a glass or ceramic host [4,5]. In this approach, the waste is usually dispersed within the matrix as discrete particles, the matrix providing mechanical integrity and a leach resistant coating (capsule) [1,4,5]. It is possible to exploit the advantages of glass-based waste forms and the radiation resistance of certain crystalline phases, for example, pyrochlore forms [6,7], by forming glass–crystal composites [5].

Recently, there has been renewed interest in using alternative processing routes to develop nuclear waste disposal forms based on vitrification by reaction sintering under pressure or hot-pressing methods [4,5,8]. The alternative process of vitrification by glass powder sintering seems, in principle, to be more advantageous than the traditional method of glass melting, basically because of lower processing temperatures (e.g. $\leq$800 °C versus 1150 °C for a borosilicate glass matrix), less volatility of radionuclides, less equipment and materials corrosion and no processing related waste loading constraints [9,10]. Moreover, phase separation in the glass does not take place at the relatively low temperatures involved. Thus, waste loading is limited only by product quality, i.e., chemical durability of the glass used and structural integrity of the glass/crystal interface [5].

In relation to these alternative waste forms, materials with fluorite and fluorite related structures such as pyrochlore ($RE_2Ti_2O_7$ or $RE_2Zr_2O_7$ with RE = rare earth) are considered attractive for accommodating radionuclides, especially actinides [6,7,11]. These crystals show a high solubility for actinides and other radionuclides because of a vacant site in the

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pyrochlore structure, which has been shown to be remarkably effective in accommodating waste ions [6,7,11]. Other reason for such interest resides in the fact that certain of these materials have been shown to be very stable against heavy ion induced amorphisation [12]. In previous studies [5,13,14], lanthanum zirconate and gadolinium zirconate particles of pyrochlore crystalline structure were embedded in lead silicate or borosilicate glass matrix for production of novel glass/crystal composite waste forms. The latest study of this composite system was done by introducing a hot-pressing process which led to good densification of composites with high loading of lanthanum zirconate particles in a lead silicate glass matrix at relatively low processing temperatures (<700 °C) [13]. Following our previous work [5], the aim of the present investigation is to explore further the new composite approach which includes the principal advantages of glasses and ceramic waste forms in order to produce materials with radionuclides incorporated within the crystalline phase, which is itself encapsulated in a glass matrix. The new composite waste forms are proposed for the immobilization of special type of radioactive wastes, in particular waste containing high concentration of actinides coming from Pu reprocessing [15].

In this study, we extend the studies on these alternative waste forms investigating gadolinium zirconate particles encapsulated in a soda borosilicate glass matrix. The fabrication of the composites involving powder mixing followed by hot pressing is presented. When considering a suitable material for hosting nuclear waste it is important to investigate also its behaviour under mechanical or thermal stresses [16,17]. Thus in the present study several mechanical tests were conducted on the new composite waste forms to assess their structural stability and fracture behaviour.

2. Experimental procedure

2.1. Starting materials

The gadolinium zirconate powder was prepared by coprecipitation synthesis from commercial powders. The process involves mixing and sintering of the powders and it is described in ref. [14]. Starting materials were gadolinium chloride ($GdCl_3 \cdot 6H_2O$) and zirconium dichloride oxide ($ZrOCl_2 \cdot 8H_2O$). Table 1 presents the most relevant physical and mechanical properties of $Gd_2Zr_2O_7$ [18]. The particle size distribution of the gadolinium zirconate powder, as measured by laser scattering technique [19], indicated that 50% of the particles had a size <60 μm while particles of up to 200 μm in size were measured.

Table 1
Physical properties of $Gd_2Zr_2O_7$ [18]

Property	
Density (g cm^{-3})	6.99
Melting point (°C)	2250
Thermal expansion coefficient (10^{-6} K^{-1})	11.6
Thermal conductivity (W/m K)	1.6
Elastic modulus (GPa)	205
Hardness (GPa)	10

Table 2
Composition and properties of the borosilicate glass matrix [10]

Composition	wt%
SiO_2	56.7
B_2O_3	12.4
Al_2O_3	2.6
Na_2O	17.5
CaO	4.1
MgO	2.1
TiO_2	4.5
Average particle size (μm)	5.5
Density (g cm^{-3})	2.57
Thermal expansion coefficient (10^{-6} K^{-1})	10.6
Elastic modulus (GPa)	73
Softening point (°C)	537

The soda borosilicate glass chosen for this investigation has been employed in previous studies on the immobilization of nuclear waste [10]. Table 2 shows a summary of relevant physical properties of the soda borosilicate glass used. Due to its soda content being higher than that in common borosilicate glasses [4], this glass has a relatively low softening point and consequently a low sintering temperature as well as a relative high thermal expansion coefficient. The thermal expansion coefficient of the glass is close to that of the pyrochlore phase (Table 1), which is advantageous for the combination of both materials in a glass matrix composite, as discussed below.

2.2. Preparation of composite samples

This project was set to investigate in detail the composite of gadolinium zirconate particles in soda borosilicate glass matrix. Six series of composite samples were obtained and the systems investigated are summarised in Table 3. During the first stage of the investigation, pressureless sintering experiments were carried out to find a suitable processing temperature and holding time for the subsequent hot-pressing process.

$Gd_2Zr_2O_7$ and glass powders were weighted in the correct proportions for each composition and placed in plastic bottles. The composite powders were either mixed in dry state or with addition of ethanol and then mixed for 30 min in a tubular mixer.

The wet powder was dried using a hot plate at about 40 °C and then crushed with pestle and mortar to destroy any remaining agglomerates. Hot pressing was carried out under vacuum with an applied pressure of 5 MPa at 620 °C, and the holding time was 2 h. A custom-made facility described

Table 3
Summary of the $Gd_2Zr_2O_7$/borosilicate glass systems investigated

Composite	$Gd_2Zr_2O_7$ (vol%)	Mixing condition
$Gd_2Zr_2O_7$/glass	40	In ethanol
$Gd_2Zr_2O_7$/glass	30	In ethanol
$Gd_2Zr_2O_7$/glass	30	Dry
$Gd_2Zr_2O_7$/glass	5	In ethanol
$Gd_2Zr_2O_7$/glass	5	Dry
Glass borosilicate matrix	0	In ethanol

elsewhere [20] was employed. The heating rate was held constant at 10 °C/min and the sample was left to cool down in the hot press.

2.3. Characterization of the composites

The density of the unsintered samples was determined geometrically and by the Archimedes' method in the case of sintered and hot-pressed samples. The results were compared with the theoretical density which was calculated using the rule of mixtures and the density values for Gd zirconate and borosilicate glass from Tables 1 and 2, respectively.

The hot-pressed samples were analysed by X-ray diffraction (XRD) (Philips PW 1719 diffractometer using Cu Kα radiation at 40 kV of voltage) to determine possible crystalline phases nucleated during processing. Polished samples and fracture surfaces were observed by scanning electron microscopy (SEM) in order to verify the densification and porosity achieved (calculated by Archimedes' principle) and to estimate the occurrence of pullout or debonding of gadolinium zirconate particles during fracture of the composites. Transmission electron microscopy (TEM) was performed on selected samples in order to investigate any bonding phase formed between the glass matrix and pyrochlore particle inclusions. In addition, TEM observations gave an extra opportunity to establish the presence of any new phases formed during hot pressing.

The hot-pressed sample containing 30 vol% Gd zirconate particles was cut into smaller specimens using a diamond saw in order to carry out different mechanical tests. The Young's modulus was measured on prismatic bars using the Grindosonic® or impulse excitation technique. Hardness and indentation fracture toughness were measured by Vickers' indentations using a load of 5 kg applied for 10 s. In addition, several hot-pressed discs were polished using diamond paste up to 1 μm finish, and subsequently cut to obtain bars of 33–38 mm length, 4 mm width and 3 mm height. These specimens were subjected to mechanical tests in order to determine the flexural strength using the three-point bending test. For the three-point bending test, the following parameters were used: distance between supports = 20 mm and test speed = 0.5 mm/min. At least five samples were tested and the results were averaged.

3. Results and discussion

3.1. Microstructural characterization

XRD analysis confirmed no traces of contamination in the powders used. Fig. 1 shows a comparison between the XRD patterns of the milled Gd zirconate powder (as-received), a sintered borosilicate glass matrix sample containing 30 vol% gadolinium zirconate (650 °C for 2 h) and a hot-pressed borosilicate glass matrix sample containing 30 vol% gadolinium zirconate (620 °C for 2 h). It can be observed that no new crystalline phases have formed during the heat-treatment as no extra XRD peaks are detected. This also indicates that no devitrification process occurred in the glass matrix at the working temperatures.

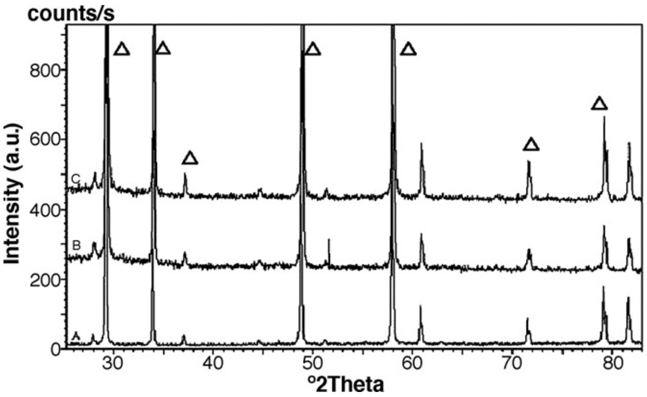

Fig. 1. XRD patterns of (A) gadolinium zirconate powder (as-received), (B) sintered borosilicate glass matrix containing 30 vol% gadolinium zirconate (650 °C for 2 h) and (C) hot-pressed borosilicate glass matrix sample containing 30 vol% gadolinium zirconate (620 °C for 2 h). No extra significant crystalline peaks due to devitrification of the glass matrix are detected, the main peaks observed correspond to the pyrochlore phase (marked).

By trial-and-error approach, it was determined that the optimal sintering temperature and holding time for the pressureless sintering of borosilicate glass/Gd zirconate particle composites were 650 °C and 2 h, respectively. In addition, it was confirmed by differential thermal analysis [19] that the powders were thermally stable during sintering, and that they did not transform to another crystalline structure over the temperature range of interest for this study (<700 °C).

The hot-pressing temperature was chosen to be slightly lower than that optimised for the pressureless sintering experiments, e.g. 620 °C instead of 650 °C. Hot-pressed samples with two concentrations of Gd zirconate particles were fabricated: 30 and 40 vol%. The sample with 30 vol% Gd zirconate inclusions resulted in a relative density of 98.2% and the 40 vol% inclusions sample had a relative density of 97.7%.

Figs. 2 and 3 show the polished and fracture surface, respectively, of a hot-pressed sample containing 30 vol% gadolinium zirconate particles. Very little residual porosity is observed in the images, which agrees with the density measurements (for this sample 98.2% relative density). The

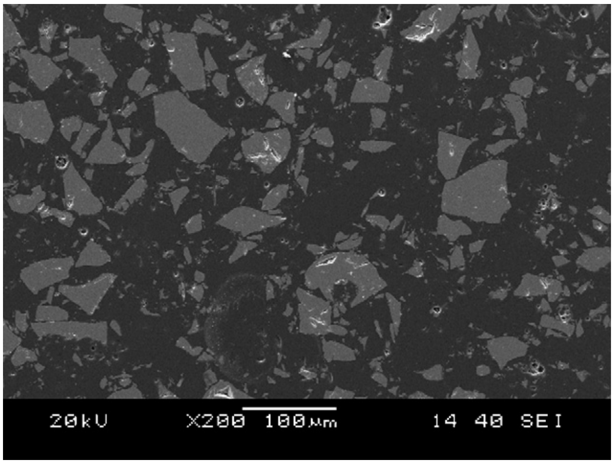

Fig. 2. SEM image of a polished surface of a hot-pressed sample containing 30 vol% gadolinium zirconate in the borosilicate glass matrix.

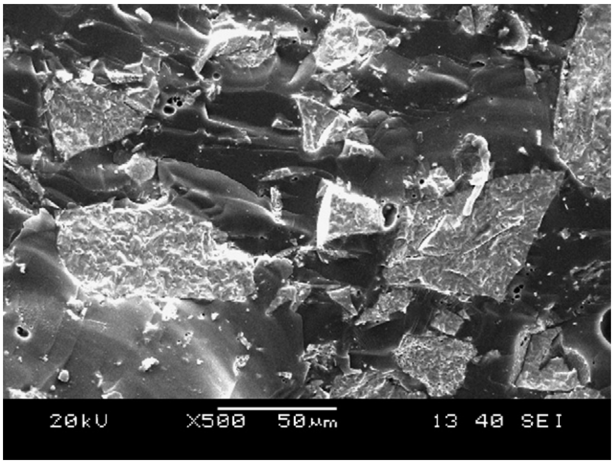

Fig. 3. SEM image of a fracture surface of a hot-pressed sample containing 30 vol% gadolinium zirconate in the borosilicate glass matrix.

limited residual porosity in the glass might be caused by trapped gases during sintering, although the pyrochlore particles contain pores themselves, which are a consequence of the manufacturing process of the powder [14]. By analysing fracture surfaces of composites it is observed that the fracture behaviour is clearly transgranular. Fig. 3 shows, for example, that the main crack has proceeded through both the glass matrix and the pyrochlore particle. This is a very clear indication of a strong bonding at the pyrochlore/borosilicate glass interface. The crack propagation observed is in agreement with the expected behaviour since the thermal expansion coefficients of the two phases are closely matched ($\Delta\alpha \cong 1 \times 10^{-6}\ \mathrm{K}^{-1}$) (see Tables 1 and 2), suppressing significantly the development of residual thermal stress in the composites upon cooling from the processing temperature. No pullout or debonding of the pyrochlore particles from the glass matrix was observed and the image of the fracture surface (Fig. 3) shows a sharp interface between the glass matrix and the pyroclore particles. The interface was further investigated using TEM. By analysing the 30 vol% $Gd_2Zr_2O_7$/glass composite using TEM no chemical interactions or formation of new intergranular phases at the interfaces between the glass matrix and the pyrochlore inclusions were detected. As can be seen in Fig. 4, a ‘‘clean’’ interface exists between the pyrochlore particle and the glass matrix that rules out chemical reactions occurring at the interface. These facts are extremely favourable regarding the mechanical integrity and chemical stability of the composite samples which are the main requirements for optimal nuclear waste forms. The presence of ‘‘weak’’ or thermodynamically unstable interfaces would make the material unsuitable for this application as nuclear waste form.

3.2. Mechanical properties

Mechanical tests were conducted on hot-pressed samples containing 30 vol% $Gd_2Zr_2O_7$. To determine the Young's modulus the Grindosonic® test was used. A value of $E = 98 \pm 2$ GPa was measured. The result indicates that addition of pyrochlore particles increases the Young's modulus of the monolithic glass.

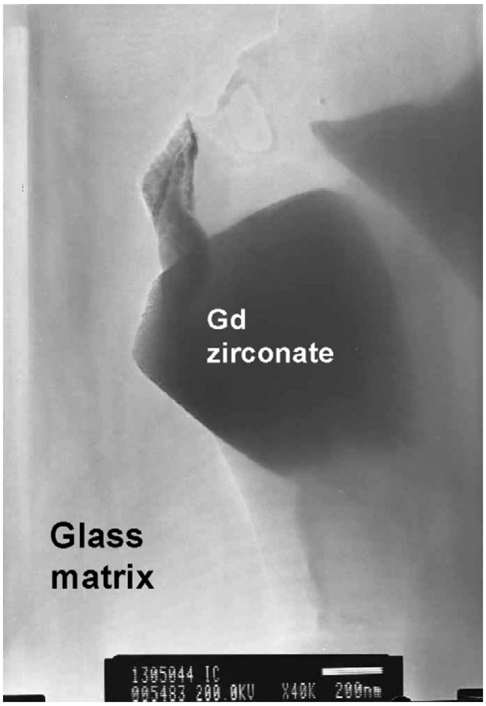

Fig. 4. TEM image of a pyrochlore particle (dark area) surrounded by the borosilicate glass matrix. There is no indication of chemical reaction at the interface between the two materials.

The result is in fair agreement with the rule of mixtures, which would give a value $E = 112$ GPa, considering that the sample contains a given amount of porosity.

The flexural strength of the composite with 30 vol% Gd zirconate, determined on five samples by a three-point bending test, was found to be: $\sigma_{\mathrm{flex}} = 103 \pm 9$ MPa. This is a relatively high value compared with other ceramic waste forms, like for instance the unreinforced borosilicate glass (≅60 MPa) [21], pointing to an acceptable mechanical behaviour of the glass–pyrochlore composite material.

The hardness of the composite with 30 vol% Gd zirconate, determined by Vickers indentation, was found to be: $H = 7 \pm 1$ GPa. In order to measure the indentation fracture toughness (K_{IC}) of the composite, several indentations were produced on polished samples, the length of cracks emanating from the indentations was measured and K_{IC} was calculated by the equation proposed by Evans and Charles [22]. A value $K_{\mathrm{IC}} = 1.7 \pm 0.2\ \mathrm{MPa\ m}^{-1/2}$ was determined. This value is higher than K_{IC} of plain borosilicate glass, which has been measured to be of the order of $0.7\ \mathrm{MPa\ m}^{-1/2}$ [21,23]. This is a significant result, as it demonstrates that $Gd_2Zr_2O_7$ inclusions impart a reinforcing (toughening) effect. Hence the composite should exhibit a higher tolerance to fracture in comparison to the plain borosilicate glass matrix. Observation of fracture surfaces (e.g. Fig. 3) reveals that in the composite material fracture propagates through both the glass matrix and $Gd_2Zr_2O_7$ particles with little crack deflection at glass/$Gd_2Zr_2O_7$ interfaces. The possibility of toughening brittle matrices by ceramic particles, as it occurs in the present composites, has been demonstrated in a previous study [24], the condition being that a strong interface between the matrix and the included particles must be achieved, as it is the case in the present system.

The brittleness index ($B = H/K_{IC}$) of the composite material with 30 vol% $Gd_2Zr_2O_7$ has a value $B = 4.11\ \mu m^{-1/2}$, which is about 40% lower than the value for plain borosilicate glass [25]. The brittleness index measures the relative resistance of the material to crack propagation and deformation under contact loads [26] and it can be used, for example, as a figure of merit to determine the relative resistance of different materials to impact loads. Thus, it is possible to conclude that in general the composite material developed here will have increased fracture tolerant behaviour and better resistance to impact loads than monolithic borosilicate glass waste form, due to its reduced brittleness. The chemical durability of the composite material in contact with water and the comparison of its leaching behaviour with that of monolithic borosilicate glass waste forms is the focus of current studies.

4. Conclusions

Soda borosilicate glass matrix composites containing $Gd_2Zr_2O_7$ pyrochlore particles were developed and they are proposed as alternative nuclear waste forms. As indicated by previous work [6,7,11], the pyrochlore phase should act as an efficient host for actinides and for Pu. The composites were manufactured by powder mixing (wet and dry) followed by hot pressing at relatively low temperatures (620 °C). The densification was found to be >98% of theoretical density in composites with a relatively high volume fraction of gadolinium zirconate particles as inclusions (30 vol%). The composites were found to exhibit relatively high mechanical strength, Young's modulus as well as high hardness values in comparison to monolithic borosilicate glass. The indentation fracture toughness and the brittleness index were found also to improve in the composites, which indicates that the composite waste form will exhibit a higher resistance to impact loads and to contact deformation than monolithic borosilicate glass waste forms.

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