J Mater Sci (2008) 43:4152–4156
DOI 10.1007/s10853-007-2232-3

REES RAWLINGS FESTSCHRIFT

Hot-pressed phosphate glass–ceramic matrix composites containing calcium phosphate particles for nuclear waste encapsulation

E. M. Michie · R. W. Grimes · A. R. Boccaccini

Received: 28 July 2007 / Accepted: 15 October 2007 / Published online: 3 April 2008

Abstract Sodium aluminium phosphate (NaAlP) glass–ceramic composites were produced as potential wasteforms for the immobilization of special categories of halide-containing radioactive waste. Sintering conditions for encapsulating a simulated waste (a calcinated mixture of calcium phosphate host and various oxides) in the cold-pressed NaAlP glass–ceramic were first determined and the results were compared with similar samples prepared by hot pressing. In both cases, the conditions aimed to provide a very high-density material, via as low production temperatures as possible, in conjunction with a high waste loading (75 wt.% simulated waste to 25 wt.% glass). It was found that by hot pressing and using a NaAlP glass–ceramic containing 2 mol% B_2O_3, significantly lower temperatures could be employed compared to the cold pressing and sintering route. The lowest temperature at which a sufficiently dense hot-pressed product was achieved (86% theoretical density), that exhibited mechanical properties similar to those of borosilicate glass (e.g. Young's modulus 67 ± 2 GPa), was 550 °C. This processing temperature is considerably lower than values reported in the literature for similar systems. As such, hot pressing can be considered as a convenient technique for the fabrication of this type of composite for waste encapsulation.

Introduction

The choice of host material for radioactive waste immobilization depends upon both the chemistry of the waste type and the physical environment in which the wasteform is to be stored [1, 2]. With societal pressure to clean-up and safely manage the storage of a wide variety of legacy radioactive wastes, there is a growing incentive to develop new wasteforms. In particular, although borosilicate glass can be used to immobilize waste from conventional irradiated (spent) uranium oxide fuel and certain defence wastes, alternatives are required to accommodate more unusual waste streams.

Radioactive waste immobilization is essentially achieved via two main routes. The first involves the dissolution of waste elements within the host lattice, thus incorporating radionuclides and other waste components into a host matrix at the atomic scale. The second route is the encapsulation of the waste phase within an inert and protective matrix, incorporating it as a separate phase and thereby forming a composite [1].

Glass is a favourable host as it can be used to dissolve wastes forming a homogeneous and castable product [1]. Importantly, glass has reasonably low processing temperatures, and can demonstrate the required chemical durability. Furthermore, glasses can adapt to changes brought on by the radioactive decay of waste elements [4]. This is because they are tolerant to variations in waste composition and are capable of including a range of elements, produced as fission products, into their network structure.

For radioactive waste applications, a completely amorphous glass, with no crystallization, is usually desired when crystallization can impair the structural integrity and chemical durability of the waste form. Therefore, the critical cooling rate for glass formation should be low and the glass should exhibit a high glass transition temperature and high thermal stability. The solubility of actinides and chlorides in silicate-based glasses is, however, relatively low, normally under 5% for actinides and under 1.5% for chlorides [3, 4]. Waste loading with high levels of chloride

E. M. Michie · R. W. Grimes · A. R. Boccaccini (✉)
Department of Materials, Imperial College London,
South Kensington Campus, London SW7 2AZ, UK
e-mail: a.boccaccini@imperial.ac.uk

ions can consequently lead to phase separation in silicate glasses, which is detrimental to the properties of the wasteform. Therefore, for these types of waste, alternatives to borosilicate glass are required.

Calcium phosphate ceramics based on the mineral phases chloroapatite $Ca_5(PO_4)_3Cl$ and spodiosite $Ca_2(PO_4)Cl$ are known to be very effective for the immobilization of waste derived from the pyrochemical reprocessing of Pu metal [5]. These ceramic phases alone are not a suitable wasteform, however, they are in the form of particulate products and therefore require further processing; for example, encapsulation in an inert glass matrix (e.g. a phosphate glass) in order to produce a monolithic glass–ceramic composite wasteform.

The solubilities of actinide oxides in phosphate glasses are significantly higher than the solubilities found for borosilicate glasses [2]. This indicates that phosphate compositions could be suitable candidates for the immobilization of waste arising from the pyrochemical reprocessing of Pu, where levels of actinides and chlorides are significantly higher [3, 5, 6]. New phosphate glass–ceramic waste forms fabricated by a pressureless sintering process have been investigated previously [3, 5–8]. In particular, a sodium aluminium phosphate-based glass has been proposed for the immobilization of special categories of radioactive waste. The glass transition temperature for sodium aluminium phosphate (NaAlP) glass is 405 °C. The glass exhibits two crystallization exotherms, at 504 °C and 607 °C, which correspond to the formation of a mixture of crystalline phases. In order to reduce or prevent this devitrification, a network modifier such as B_2O_3 can be used. Small amounts of B_2O_3 added to NaAlP glass have been shown to greatly improve the thermal stability and increase its resistance to crystallisation, with little or no effect on its chemical durability [8].

Pressureless sintering requires relatively high temperatures, which can lead to phase separation and crystallisation, thereby reducing the chemical durability of the material, perhaps leading to enhanced leaching of radiotoxic species [5]. In this article, a process based on hot pressing has been proposed for this system, which aims to reduce the processing temperatures required. Previous research on other glass–ceramic systems has found that hot pressing has the potential to immobilize nuclear waste in composite materials [9, 10] that are more dense than those fabricated by pressureless sintering [11].

Experimental procedure

Simulated waste

A dry calcined mixture of a calcium phosphate host containing various oxides was used. The composition of the simulated waste is given in Table 1. Details of the simulated waste preparation can be found in previous literature [3], and the technology discussed here is in principle applicable to dry waste. The density of this waste, derived using a helium pycnometer, was 3.30 g/cm^3. The particle size of the powder was measured using a Teepol apparatus (Malvern Instruments SB.0D) with a 45-mm lens. The particle distribution was bimodal with 90% of the particles larger than 2 μm, with a mean size of approximately 20 μm, and 10% of particles smaller than 2 μm with a mean size of about 0.4 μm.

Table 1 Chemical composition of the calcined non-radioactive simulant waste

Component	Content (wt.%)
HfO_2	20.7
Ga_2O_3	28.0
Al_2O_3	9.8
Sm_2O_3	4.6
MgO	6.3
FeO	1.3
Ta_2O_5	1.3
NiO	1.3
CaF_2	10.4
KCl	16.3

Sodium aluminium phosphate glass

Two different sodium aluminium phosphate glass compositions were investigated: one which contained no additives (NaAlP) and one which contains 2 mol% of B_2O_3 (NaAlP-B). The compositions of the glasses are given in Table 2. The glasses were formed from di-sodium hydrogen phosphate, aluminium oxide and aluminium phosphate. Details of the glass preparation can be found in the previous literature [7, 8]. The helium pycnometer density of the NaAlP glass was 2.63 g/cm^3. Particle size analysis of the glass powders after grinding the glass frits, undertaken with a 100-mm lens, indicated a normal distribution with a maximum between 30 and 40 μm and with 90% of the glass particles found to be smaller than 80 μm.

Table 2 Chemical composition of the two encapsulation glasses (mol%)

Glass	Na_2O	Al_2O_3	P_2O_5	B_2O_3
NaAlP	40.8	19.4	39.8	–
NaAlP-B	40.0	19.0	39.0	2.0

Cold pressing and pressureless sintering

The waste simulant and dry glass powder were mixed in proportions 75 wt.% to 25 wt.%, respectively. Mixing was carried out for 5 h using an automatic tumbler. Powder compacts of the glass powder and waste simulants were then prepared under a pressure of 125 MPa, using a 10 mm diameter, hardened tool steel compaction die. The pellets were sintered in an electric furnace, in air, for 4 h at different temperatures. Heating and cooling rates were set at 10 °C/min. Mass and dimensions of each compact were measured before and after sintering using Vernier callipers. From these measurements of thickness and diameter, the volumetric % shrinkage was calculated. The hardness was measured by Vickers indentations. A load of 5 kg was applied for 10 s for all samples, except those containing the glass NaAlP-B, which were sintered at 550 °C and 600 °C, where a load of 3 kg was applied for 10 s.

Hot pressing and mechanical characterisation

Hot-pressed samples were also prepared using a dry mix of 75 wt.% simulated waste and 25 wt.% glass powder. A custom-made electrically heated hot-press was used [12]. The diameter of the carbon die for hot pressing was 38 mm. All parts of the die were cleaned and each sample was lubricated using a boron nitride aerosol spray. The samples were heated at a rate of 10 °C/min. A pressure of 10 MPa was applied as soon as the sintering temperature was reached, in the range (500–680 °C). The cooling rate was set at 100 °C/h. Pressure was removed over ~30 s. Sample densities were determined geometrically. Young's modulus was measured by the impulse excitation technique, which subjects the sample to an initial deformation by means of a mechanical bending impulse, producing a transient mechanical vibration in the sample. The frequency of the vibration is related to the mass of the sample and its stiffness. Stress–strain behaviour was assessed by measuring the flexural strength applying a 3-point bend test. Rectangular bars were bent under an applied load until fracture occurred (the mean height and width of the bars were 3.49 and 3.08 mm, respectively). The distance between the supports was 20 mm, and a test speed of 0.5 mm/min was used. The hardness of all hot-pressed samples was measured by Vickers indentations. For each test a load of 5 kg was applied for 10 s.

Results and discussion

A comparison of the processing temperatures and measured hardness and density values of the pressureless sintered and hot-pressed samples is presented in Table 3.

Cold pressing followed by sintering led to materials which were highly porous (see Fig. 1) and exhibited very low hardness, indicating that these specimens would exhibit generally poor mechanical properties. Higher processing temperatures could be used in order to achieve sufficient densification. However, raising the processing temperature is not desirable because of the thermal instability of the mineral phases present in this system [13]. Higher temperatures would also increase the cost of production. Alternatively, since the viscosity of the glass–ceramic increases with the volume fraction of crystalline phases [14], higher densities could also be achieved at low concentrations of the simulated waste, but this is also undesirable from the point of view of the efficiency of the encapsulation method.

Previous work [6] has shown that samples made with the same composition of glass and waste, cold pressed at 69 MPa and sintered for 4 h at 750 °C, yielded densities of 80–83% theoretical. The particle size of the glass employed was <45 μm, similar to the powders used in the present study. The density achieved is comparable to the density of the equivalent cold-pressed and sintered samples from this study (see Table 3).

For the hot-pressed materials, processing at the lower temperature of 550 °C achieved sufficient densification (>80%) and as a result improved mechanical properties, as evidenced by the hardness values given in Table 3. Data for Young's modulus and flexural strength are shown in Table 4. The Young's modulus of the hot-pressed sample is comparable to that of borosilicate glasses which is typically 60 GPa. It can be anticipated that the Brittleness index ($B = H/K_{Ic}$, with H = hardness and K_{Ic} = fracture toughness [15]) of this material, which measures the relative resistance of the material to crack propagation and deformation under contact loads, would be similar to or better than that of monolithic borosilicate glass due to the potential higher fracture toughness of the glass–ceramic composite [16]. Although it is not an official acceptance criterion for waste disposal, the Brittleness index (B) can be used, for example, as a figure of merit to determine the relative resistance of different materials to impact loads.

Various phases were identified within the pressureless sintered and hot-pressed composites. Figure 2a shows an SEM micrograph of the microstructure of a sample hot-pressed at 550 °C under 10MPa. Isolated metal oxide phases were observed to be homogeneously distributed throughout a glass–ceramic matrix. Figure 2a also shows the impression left by the Vickers indentation test. In Fig. 2b, it can be seen that crack propagation, from the Vickers indentation, runs through different phases and inclusions, and not along the interfaces. This demonstrates an excellent adhesion/bonding between the glass–ceramic matrix and the simulated waste.

Table 3 Processing temperatures, hardness and density measurements of the pressureless sintered and hot-pressed samples

Sample	Temp (°C)	Pressure (MPa)	Vickers Hardness (GPa)	Percentage of theoretical density (%)
Glass NaAlP				
Pressureless sintered	800	–	1.6 ± 0.4	87
	750	–	1.5 ± 0.2	78
	700	–	1.5 ± 0.2	77
Hot-pressed	680	5	4.0 ± 0.3	93
	650	10	3.5 ± 0.1	90
	610	15	3.2 ± 0.5	96
Glass NaAlP-B				
Pressureless sintered	650	–	1.4 ± 0.2	75
	600	–	0.4 ± 0.2	62
	550	–	0.4 ± 0.1	58
Hot-pressed	550	10	3.2 ± 0.5	86
	500	10	3.0 ± 0.5	71

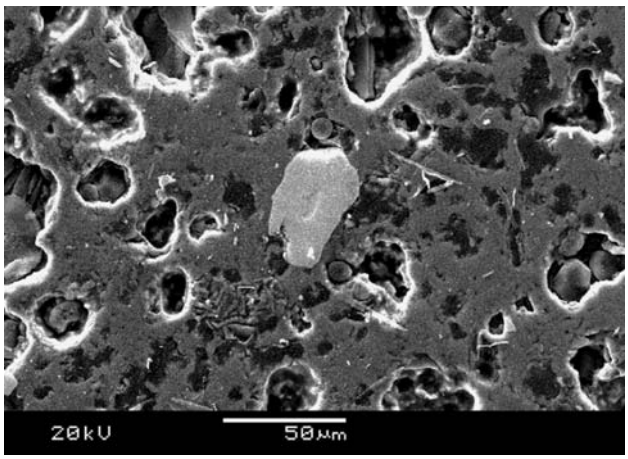

Fig. 1 SEM image of a sample containing 25 wt.% NaAlP-B glass pressureless sintered at 550 °C

In the hot-pressed samples both glasses underwent a certain degree of crystallisation, forming a glass–ceramic matrix. Unless the crystalline phases formed are less durable than unreacted NaAlP glass or the phases adversely affect any surrounding NaAlP glass, the crystallized phases are not considered to be detrimental to the properties of the final waste form.

XRD analysis revealed a complex fluorite-related structure with other minor phases, as shown in the XRD spectra presented in Fig. 3. A sample containing NaAlP-B hot-pressed at 550 °C under 10 MPa is compared to the spectra generated by a sample containing NaAlP at 650 °C under 10 MPa. An identical material has been produced with little effect of the B_2O_3 additions to crystallisation evident. The fluorite related structure was found to be flouroapatite $Ca_{10}(PO_4)_6(F)_2$ (ICDD file No. PDF # 9-432). Not all the peaks were matched precisely. This is due to other minor phases being present including $AlPO_4$, which was also observed in the SEM analysis.

The formation of halite observed in some of the earlier studies is clearly undesirable, as this phase is detrimental to the chemical durability of the material. In the current investigation, no evidence for the formation of a separate halite phase was found under any of the processing parameters tested. This absence is anticipated since the composition of the waste simulant powder used in this study does not contain a high concentration of chlorides, as opposed to some of the other waste streams previously investigated [5]. In agreement with this previous work it is therefore less likely that a halite phase would form. The lower processing temperatures used would also tend to prohibit its formation.

Another important factor in determining the integrity of a waste form is the chemical durability. After generating samples with appropriate mechanical properties at these lower temperatures, a future step would be to measure leaching rates of the samples. Another consideration should

Table 4 Mechanical properties of the hot-pressed NaAlP-B samples

Sample	Temp (°C)	Pressure (MPa)	Young's modulus (GPa)	Max applied load (N)	Flexural strength (MPa)
Hot-pressed	550	10	67 ± 2	50 (±4)	40 (±4)
	500	10	26 ± 2	17 (±1)	14 (±1)

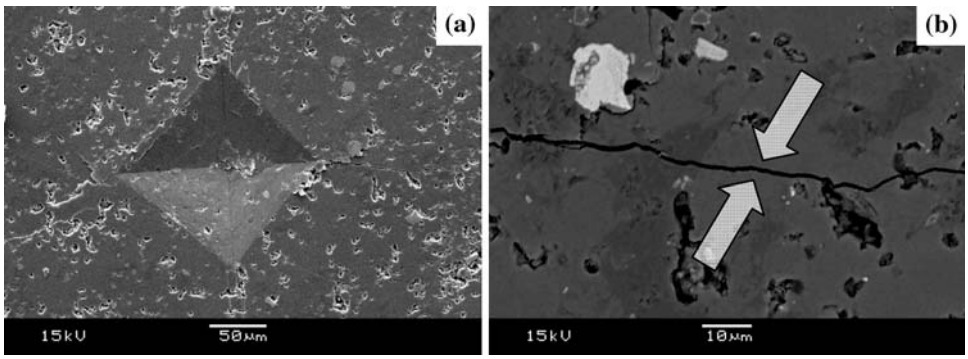

Fig. 2 SEM images of a sample containing 25 wt.% NaAlP-B glass, hot-pressed at 550 °C under 10 MPa showing (**a**) Vickers hardness indentation with cracks originating from it, (**b**) an advancing crack produced by a Vicker's indentation (highlighted by the arrows)

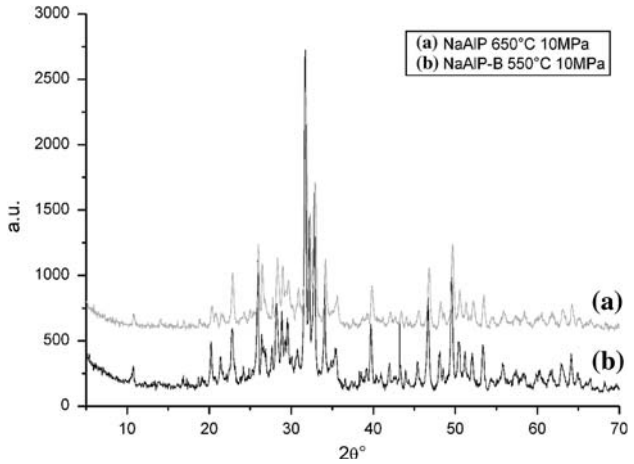

Fig. 3 XRD spectra comparing crystal phases present in samples using (**a**) NaAlP hot-pressed at 650 °C under 10 MPa and (**b**) NaAlP-B hot-pressed at 550 °C under 10 MPa. ICDD file No. (PDF # 9-432)

be how much of the chlorides are retained within the structure in order to access volatilization of chlorides during the hot-pressing process. As with previous studies [3, 5], the variation of waste loading and compositional variation in waste should also be addressed. The chemical durability of the hot-pressed composite materials fabricated here and the comparison of their leaching behaviour with that of previously developed NaAlP-based wasteforms is the focus of on-going studies.

Conclusions

It was found that for composites of NaAlP doped with B_2O_3 glass containing 75 wt.% simulated waste, pressureless sintering at 650 °C and 600 °C gave reasonable densities of up to 75% theoretical.

By hot pressing the same powder mixtures under a pressure of 10 MPa processing temperatures could be significantly reduced. Samples hot-pressed at 550 °C achieved 86% theoretical density coupled with adequate mechanical properties; for example, a Young's modulus of 67 GPa, Vickers hardness of 3.2 ± 0.5 GPa and flexural strength of 40 ± 4 MPa. Hot pressing at 500 °C yielded a more porous material, with poorer mechanical properties, indicating that 500 °C is a too low processing temperature.

Adjustments to the holding time and pressure may improve these results further, and will form the basis of further studies. It is tentatively concluded that hot pressing may be a viable method for processing this type of wasteform at a significantly lower temperature than required by the cold pressing and sintering route.

Acknowledgements This work was carried out as part of the TSEC programme KNOO and as such we are grateful to the EPSRC for funding under grant EP/C549465/1. We are particularly grateful to Brian Metcalf, Ian Donald and Shirley Fong of AWE Aldermaston (UK) for invaluable discussions and who suggested this study.

References

1. Ojovan MI, Lee WE (2005) An introduction to nuclear waste immobilisation. Elsevier Ltd., Oxford, UK
2. Donald IW, Metcalfe BL, Taylor RNJ (1997) J Mater Sci 32(22):5851
3. Metcalfe BL, Fong SK, Donald IW (2004) In: Oversby VM, Werme LO (eds) Materials research society symposium proceedings, vol 807. Warrendale, PA, pp 255–260
4. Ewing RC (1999) Proc Natl Acad Sci 96(7):3432
5. Donald IW, Metcalfe BL, Fong SK, Gerrard LA, Strachan DM, Scheele RD (2007) J Nucl Mater 361(1):78
6. Donald IW (2004) Discovery: Sci Technol J AWE 9:2
7. Metcalfe BL, Donald IW (2004) J Non-Cryst Solids 348:225
8. Donald IW, Metcalfe BL, Fong SK (2006) J Non-Cryst Solids 352:2993
9. Raman SV (1998) J Mater Sci 33(7):1887
10. Pace S et al (2005) J Nucl Mater 341(1):12
11. Boccaccini AR, Berthier T, Seglem S (2007) Ceram Int 33:1231
12. Saewong P (1998) PhD Thesis, Department of Materials, Imperial College, London, pp 45–47
13. Morton RD (1961) Norsk geologisk tidsskrift 41:223
14. Boccaccini AR, Riaz S, Moisescu C (2001) J Mater Sci Lett 20(19):1803
15. Lawn BR, Marshall DB (1979) J Am Ceram Soc 62:347
16. Boccaccini AR (1997) J Mater Process Technol 65:302