Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 358 (2006) 1–9
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Immobilization of inert TRISO-coated fuel in glass for geological disposal

Abdesselam Abdelouas *, Samuel Noirault, Bernd Grambow

SUBATECH, EMN-IN2P3/CNRS-Université de Nantes, 4, rue Alfred Kastler – La chantrerie, BP 20722, 44307 Nantes cedex 3, France

Received 13 October 2005; accepted 14 April 2006

Abstract

Vitrification of TRISO-coated gas reactor fuel particles was achieved via two methods: glass melting and sintering. Inert TRISO-coated fuel particles and a borosilicate glass were used. With glass melting at 1200–1300 °C floatation and decomposition of carbon and silicon carbide occurred. Thermal pre-treatment of the particles for oxidation of pyrocarbon did not improve the coating properties of the glass. During cooling most of the particles floated and sorbed on the crucible or mold walls. The sintered glass at 700 °C showed better coating properties of the TRISO-coated fuel particles despite higher porosity compared to glass made by melting. Aqueous leaching properties of glass with particles are similar regardless the mode of fabrication, indicating the good chemical durability of the sintered glass. Sintered glasses may constitute a good technique for TRISO-coated fuel particles immobilization for an eventual deep geological disposal.

1. Introduction

High temperature gas cooled reactors (HTR) are receiving more interest around the world due to their advantages including high thermal efficiency and safety advantages due to low-power density and large thermal capacity of the core [1,2]. Development of these reactors is being conducted in Germany, China, Russia, South Africa, United States, United Kingdom and Japan [2]. HTRs use sub-mm sized coated fuel particles embedded in the graphite matrix of fuel pebbles or block type fuel. The small fuel particles (kernels) surrounded by buffer carbon (BC), inner pyrolytic carbon (IPyC), silicon carbide (SiC) and outer pyrolytic carbon (OPyC) [3,4] are called 'TRISO fuel particles'. All coatings are designed to better confine gaseous and metallic fission products formed during the operation of the reactor.

Up to today and over the last 30 years works on TRISO-fuel particles were conducted for fuel fabrication technologies, fuel testing and performance under irradiation conditions [1–12]. Hence, in Germany the fabrication process of the fuel is so strict that only about a 100 defects were found in 3.3 million particles produced [11]. For a HTR power plant (with a thermal output of 200 MJ s^{-1}) and below

---

* Corresponding author. Tel.: +33 02 51 85 84 62; fax: +33 02 51 85 84 52.
E-mail address: abdesselam.abdelouas@subatech.in2p3.fr (A. Abdelouas).

0022-3115/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2006.04.015

1620 °C the TRISO-particles with SiC were found to ensure a high confinement of fission products [11]. Higher temperatures treatments of TRISO-particles (up to 2100 °C) have shown a 4–5 order of magnitude increase in Xe-133, I-131 and Cs-137 release [13,14] due to SiC deterioration. In Japan, TRISO-particles with zirconium carbide (ZrC) showed better confinement properties at high temperature compared to particles with SiC [15].

In Germany and the United States reprocessing of fuel for ^{233}U extraction constituted a recycling option since the 1960s. In Germany reprocessing of fuel was successful at a semi-technical test facility to make ^{233}U fresh fuel [2,16]. However, for non-proliferation aspects the reprocessing option was terminated in early 1980s. Merz et al. [16] demonstrated that the fuel particles embedded in the graphite matrix of the fuel pebbles could be directly stored in a salt mine in Germany. However, the direct disposal of fuel pebbles requires a very large disposal volume and more compact disposal configurations seem to be beneficial.

In the present work, we report on the immobilization of TRISO-UO_2 particles in glass for an eventual geological disposal. The glass constitutes an additional barrier for particles protection against groundwater corrosion and radionuclides dispersion in environment. Industrial glasses were proven to be efficient matrixes for fission products and actinides immobilization in most of the countries reprocessing civilian and military spent nuclear fuels (France, Germany, Belgium, United Kingdom, United States, Japan, Russia, etc.) [17]. The main objective was to study the feasibility of embedding the TRISO particles in glass matrix. Optimization of process and determination of the maximum load of TRISO particles in the glass are not parts of this work.

2. Materials and methods

Inert TRISO-UO_2 fuel particles were supplied by Forschungszentrum of Jüllich, Germany within the framework of the European project 'Raphael: reactor for process heat, hydrogen and electricity production' (Fig. 1). The overall diameter of the particles is 895 ± 11 µm and density measured by helium picnometry is $3.59 \pm 0.1\%$ g cm^{-3}. The glass used for particles immobilization is a borosilicate glass provided by CEA and that is being used as glass matrix for long-lived high-level waste vitrification in France; the R7T7 glass (Table 1). The glass density is 2.48 g cm^{-3}, T_g is 528 ± 8 °C and the melting temperature is about 1200 °C. The glass was used in the form of two powders prepared by CEA: $\varnothing < 63$ µm and 40 µm $< \varnothing <$ 140 µm corresponding to a BET surface area of 0.49 and 0.27 m^2 g^{-1}, respectively. The procedure of glass powder preparation can be found in [18].

2.1. Vitrification by melting

The glass powder was melted under oxic conditions in an alumina crucible placed in a high temperature furnace at 1250–1300 °C during 30 min for complete degassing. The TRISO-particles were then added to the melt right before pouring into a stainless steel mold ($35 \times 22 \times 10$ mm^3). Melting of the glass powder in presence of TRISO-particles lead to a deterioration of the fuel coatings. For each batch we used 10–20 TRISO-particles together with 5 g of glass powder. Samples ($10 \times 10 \times 1$ mm^3) were cut from the 'glass + TRISO-particles' composite and were polished down to 3 µm for microscopy and leaching experiments. Detailed observation of the glass/TRISO particle interface was conducted.

2.2. Vitrification by sintering

Sintered glasses offer several advantages in particular low processing temperatures. Glass powder and TRISO-particles were mixed before pressing at 400 bars. The resulting pellets were placed on an alumina plate in a furnace and the temperature was raised above the T_g up to 700 °C for a few minutes. At this temperature the pellet begins to swell and then to collapse but the porosity was significantly decreased. The temperature was then decreased and maintained at 680 °C for 3 h where sintering took place. In these experiments inert and pretreated (without OPyC) TRISO-particles were used. Composite chips were prepared for microscopy and leaching experiments.

2.3. Solid analysis

Polished 'glass + TRISO-particles' composite were analyzed under a JSM 5800 LV JEOL scanning electron microscope (SEM) equipped with a Kevex Energy Dispersive X-ray spectrometry (EDS) system. Thin sections of standard phases were used to obtain quantitative analyses. Corroded glass and composite samples were also observed under the microscope. On polished thin section the error is about ±5%.

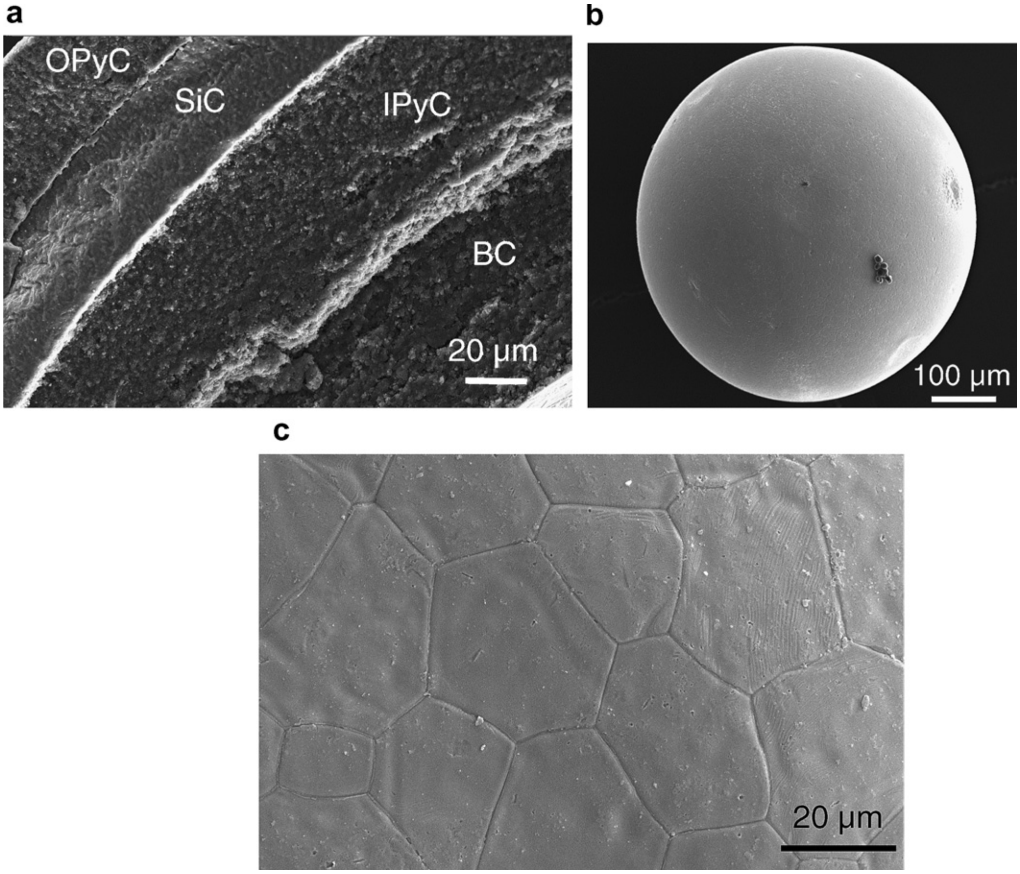

Fig. 1. SEM micrograph of a TRISO-UO_2 particle showing (a) the carbon and SiC coatings, (b) UO_2 kernel and (c) details of kernel surface.

Table 1
Chemical composition of glass used for TRSIO-fuel particles immobilization

Oxide	Wt%
SiO_2	58.84
B_2O_3	18.15
Na_2O	7.00
CaO	5.23
Li_2O	2.56
Al_2O_3	4.28
ZnO	3.24
ZrO_2	0.70
Total	100

Heat treatment of TRISO-particles for OPyC oxidation was conducted to test whether the SiC facilitates the vitrification of the particles via oxidation of Si and formation of SiO_2. The resulting SiO_2 is then supposed to sinter well with the borosilicate glass. Thermogravimetric analyses were performed using a Setaram TG-DSC 111 instrument. Oxidation experiments were conducted at 600 °C under oxygen flux for more than 20 h. Also, heat treatments were conducted at 1100 °C to obtain rapid oxidation of OPyC.

2.4. Corrosion experiments

Standard corrosion tests of ‘glass + TRISO-particles’ composite in water were conducted to test the chemical durability (quality) of the product. In addition, initial glass powder was corroded to determine the corrosion rate of the glass close to saturation of the aqueous solution (representing situations during final disposal). Experiments were conducted with glass powder or composite materials and pure water in 50 mL Teflon® containers at 90 ± 2 °C. Experiments with low surface area of glass (or composite) to solution volume (SA/V) of 10–100 m^{-1} were performed to determine the initial corrosion rate of the solid while tests conducted with $SA/V = 40.000\ m^{-1}$ aimed to determine the corrosion

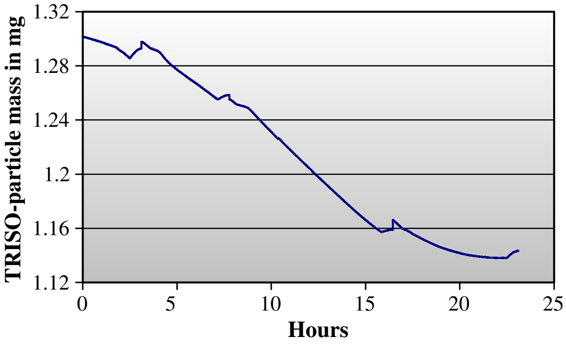

Fig. 2. Mass loss of a TRISO-fuel particle during heating at 600 °C under oxygen atmosphere (TGA).

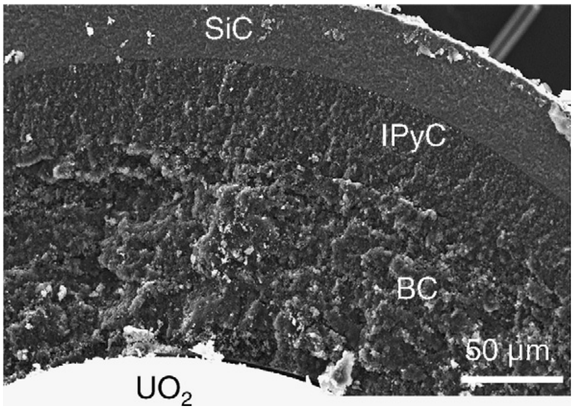

Fig. 3. SEM micrograph of a heat-treated TRISO-UO$_2$ particle showing the complete oxidation of OPyC layer.

rates at saturation conditions. In the latter case, the glass powder with diameter 40 µm < ∅ < 140 µm (BET specific surface area of 0.27 m^2 g^{-1}) was used. Tests durations ranged between 1 and 56 days.

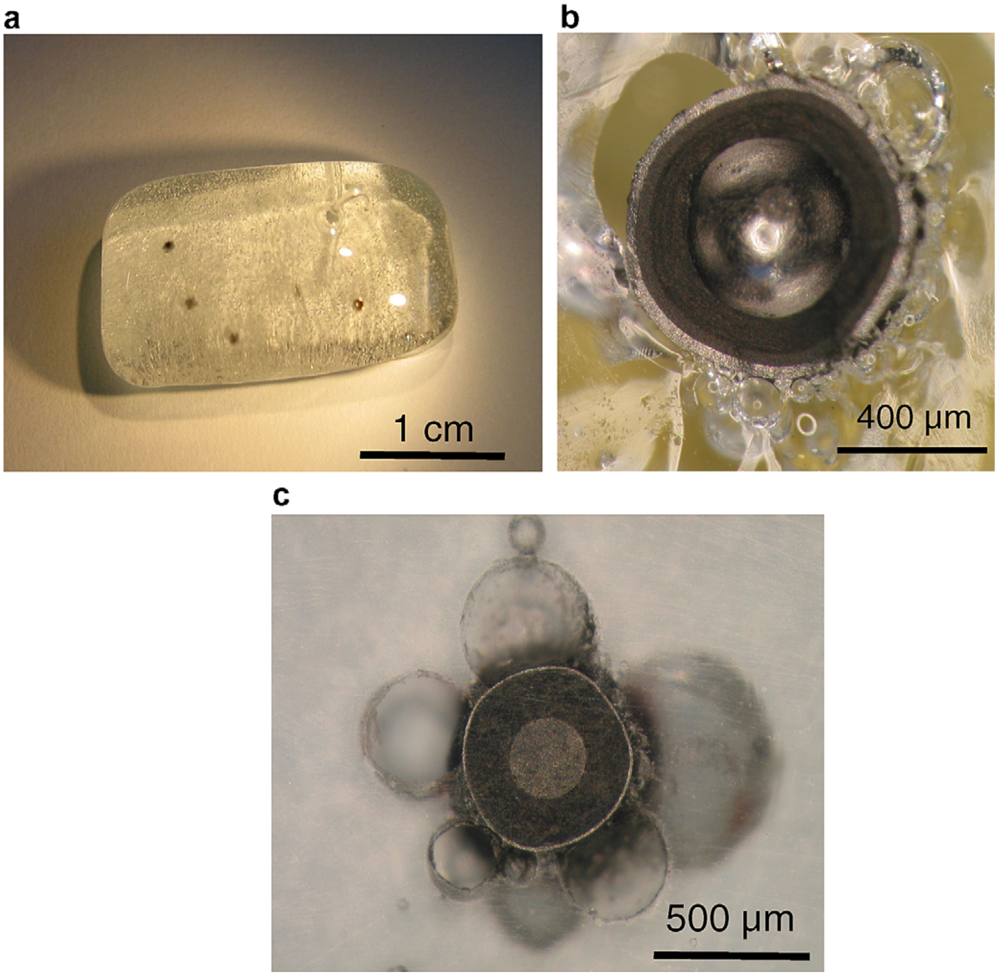

Fig. 4. TRISO-particles immobilized in melted glass (a). The TRISO-particle is surrounded by gas bubbles due to oxidation of OPyC (b) and (c).

The leached quantities of boron and lithium from the glass, used as corrosion tracers, were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with an error of ±5–10%. The normalized mass loss of the elements released from the glass were calculated with the following formula:

$$\mathrm{NL}(i) = (C_{i\_\mathrm{solution}} \times \mathrm{f_c})/(F_{i\_\mathrm{glass}} \times \mathrm{SA}/V),$$

where

$\mathrm{NL}(i)$	normalized mass loss of element i ($\mathrm{g\,m^{-2}}$)
$C_{\mathrm{i\_solution}}$	element concentration in solution ($\mathrm{g\,m^{-3}}$)
f_{c}	Conversion factor element-oxide; $f_{\mathrm{c}} =$ (oxide molar mass (in the form CO_x, where C is the cation)/element molar mass)
$F_{\mathrm{i\_glass}}$	mass fraction of element oxide in the glass
SA/V (in $\mathrm{m^{-1}}$)	ratio of the glass surface ($\mathrm{m^2}$) to solution volume ($\mathrm{m^3}$)

The thickness of the corroded glass layer was further estimated using the following relation:

$$E(i) = \mathrm{NL}(i)/d,$$

where

$E(i)$	the thickness of the corroded glass layer (μm)
$\mathrm{NL}(i)$	normalized mass loss of the ith element ($\mathrm{g\,m^{-2}}$)
d	glass density ($2.48\ \mathrm{g\,cm^{-3}}$)

3. Results

3.1. Vitrification by melting

All vitrification attempts with untreated TRISO-particles were unsuccessful because of floatation and sorption of particles on the crucible or the steel mold because the glass melt does not wet the carbon coating. Thus, the TRISO-particles were heat-treated in a TGA apparatus to remove the OPyC coating without removing the SiC layer. The results are shown in Fig. 2 as mass loss as a function of heat duration. Four cycles of heating at 600 °C over 24 h were necessary to complete oxidation of OPyC. No significant mass loss occurred between 20 and 24 h. The mass loss (0.16 mg) for a single TRISO-particle is similar to the theoretical one (0.185 mg). SEM examination of the heat-treated TRISO-particle showed the absence of the OPyC layer (Fig. 3), confirming the complete oxidation to likely carbon monoxide CO [7]. EDS analysis of the particle surface showed that the SiC layer was little affected by the oxidation as indicated by presence of only traces of $\mathrm{SiO_2}$ due to SiC oxidation. For most of the particles rapid oxidation of OPyC was obtained in a furnace heated at 1100 °C for 3 h. Complete oxidation of OPyC was confirmed by EDS analysis of the particle surface under the SEM.

Light microscope images of vitrified and untreated TRISO-particles are shown in Fig. 4. Some particles are completely embedded in the glass matrix (Fig. 4(a)) while others floated on the glass surface and caused some fracturing (Fig. 4(b)). Nevertheless, the SiC was prevented from rapid oxidation. All around the particles gas bubbles of CO [7] developed, thus increasing the mechanical stress at the glass/particle interface during cooling (Fig. 4(c)).

Detailed SEM images of the glass/particle interface are given in Fig. 5, showing large gas bubbles around the TRISO-particle. Higher magnification shows no direct contact between the glass and the

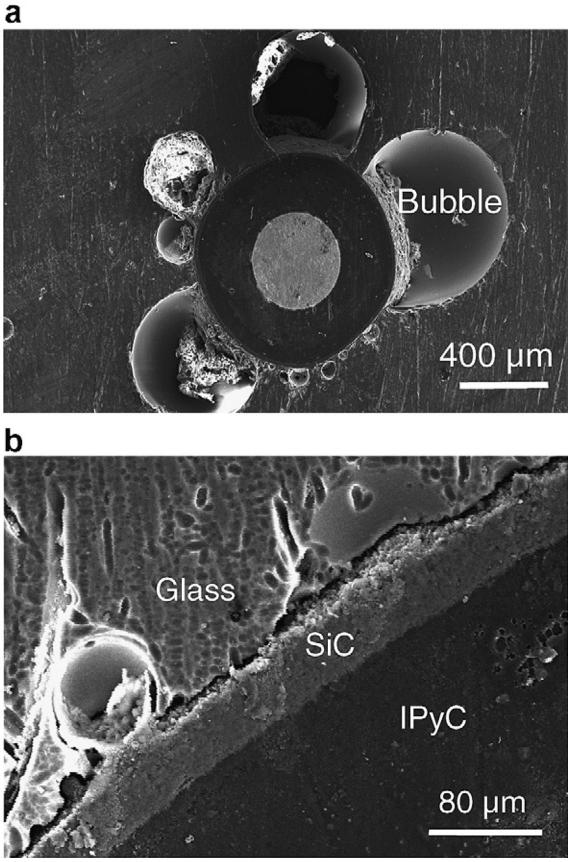

Fig. 5. SEM micograph of a TRISO-particle immobilized in melted glass (a). Interface glass/TRISO-particle (b).

SiC, which may be due to quenching revealing the difference between the thermal expansion coefficient values of glass and SiC (Fig. 5(b)). Partial oxidation of SiC and SiO_2 formation did not improve the adherence between the glass silica network and TRISO-particle surface. Fractures in the glass matrix and low coating capability of melted glass may facilitate exposition of TRISO-particles to environmental agents such as air or water humidity. Extended exposition (1–2 h) of TRISO-particles to the glass melt had led to the complete oxidation of TRISO-coatings. The remaining bare fuel kernels settled down in bottom of the crucible.

3.2. Vitrification by sintering

Because of difficulties encountered in experiments with melted glass due to high processing temperatures (1200–1300 °C), we studied the possibility of using sintered glass for TRISO-particles immobilization. The particles are expected to be stable at lower temperature ($\leqslant$700 °C). The prepared sintered glass-TRISO-particles composite can be seen in Fig. 6. Unlike the melted glass, the sintered glass presents a homogenous morphology without fractures. A cross section through the composite shows good coating properties of the glass without macroscopic bubbles around the TRISO-particle (Fig. 6(b)). The cold pressing did not cause any fractures in the particles. Furthermore, the results obtained with inert (Fig. 6(b)) and heat-treated TRISO-particle (Fig. 6(c)) are similar, suggesting that no heat treatment is necessary to immobilize the particles in the sintered glass.

SEM observation of the interface of the TRISO-particles with the sintered glass shows a direct glass

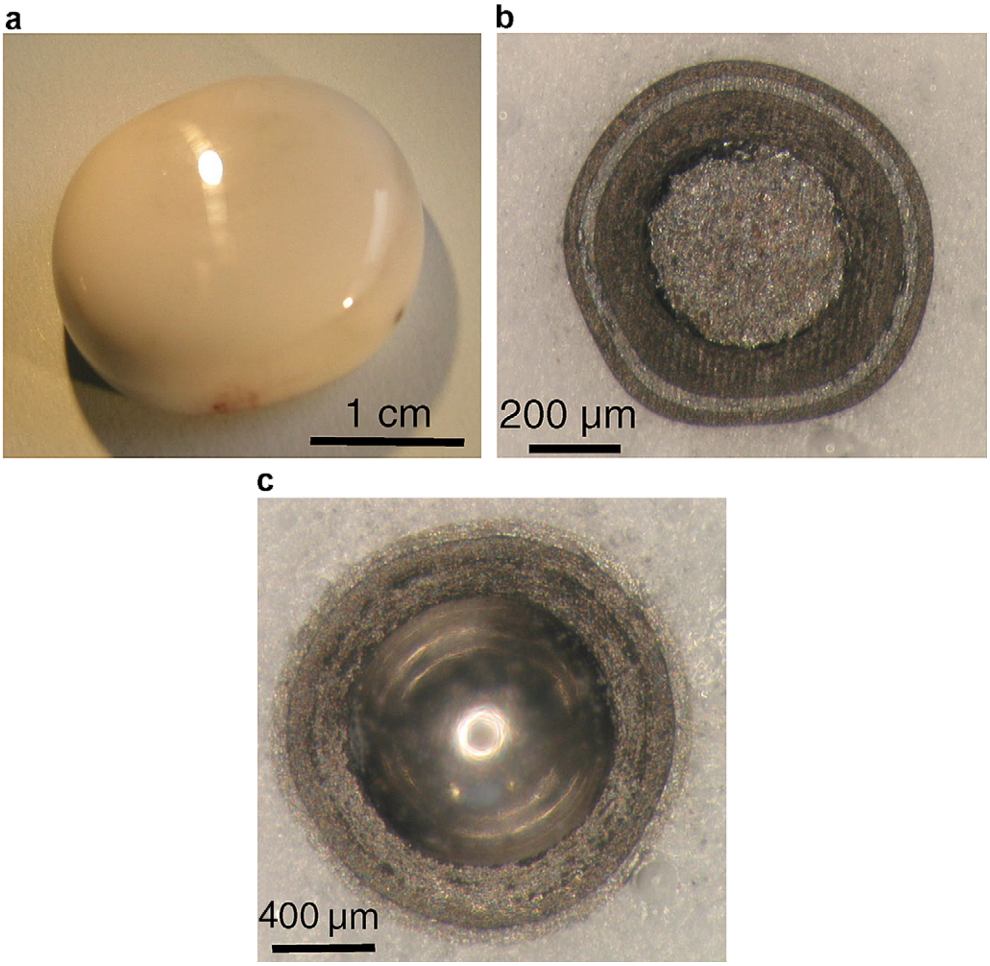

Fig. 6. Sintered glass-TRISO-particles composite (a). Inert (b) and heat-treated (c) TRISO-particle embedded in the sintered glass.

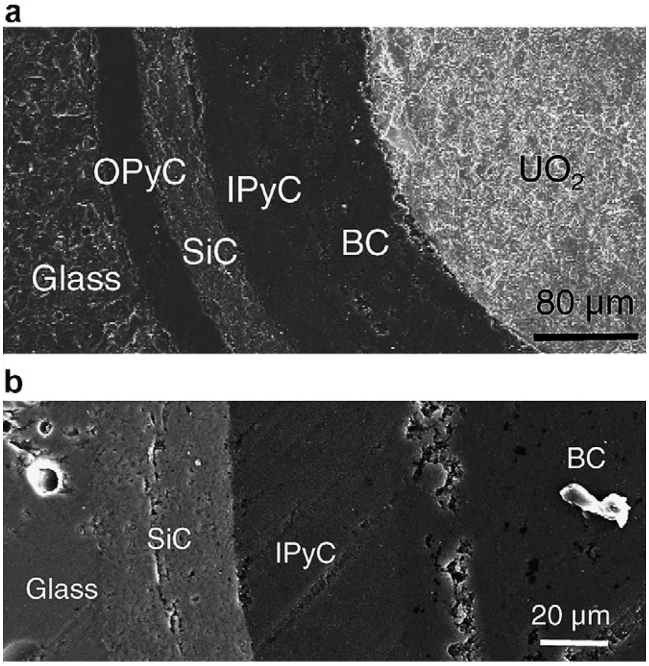

Fig. 7. SEM micrographs showing the good coating properties of the glass for the inert (a) and heat-treated (b) TRISO-particle.

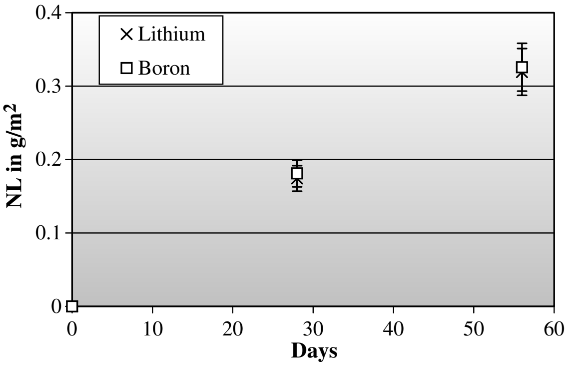

Fig. 8. Normalized mass loss of B and Li of initial glass corroded at 90 °C in pure water with SA/$V = 40.000\ \mathrm{m}^{-1}$.

coating of the OPyC (Fig. 7(a)) or the SiC (Fig. 7(b)), due to cold pressing. The sintered glass contains some remaining microporosity.

3.3. Chemical durability of melted and sintered glasses composites

Leaching experiments were conducted with initial glass powder to determine its chemical durability under near saturation conditions. The results are given in Fig. 8 in the form of normalized mass loss of B and Li as a function of time. The glass dissolution rate is $5.9 \times 10^{-3}\ \mathrm{g\ m^{-2}\ d^{-1}}$, in good agreement with results obtained by Tovena [19] for a glass with similar composition and corroded in similar conditions ($9.8 \times 10^{-3}\ \mathrm{g\ m^{-2}\ d^{-1}}$). The observed difference

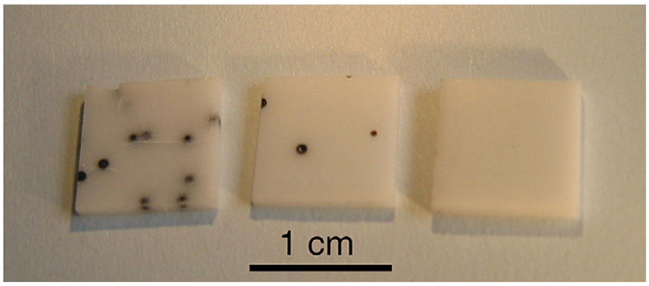

Fig. 9. Sintered glass chips with/without TRISO particles used for corrosion experiments.

may easily be a result of different surface area estimations. This dissolution rate corresponds to a total thickness of corroded glass of about 0.87 mm per 1000 years, indicating the good chemical durability of the glass at 90 °C.

Examples of sintered glass chips used in corrosion experiments are given in Fig. 9. The results of glass-TRISO-particles corrosion experiments are given in Fig. 10, which shows dissolution rates of glasses below 1 g m^{-2} d^{-1}. The dissolution rate of sintered glass is higher than that of melted glass. This can be attributed to underestimation of calculated geometric surface area due to the presence of microporosity in sintered glass. Nevertheless, both dissolution rates of composite products are similar or a little lower than those obtained for glasses with similar compositions [19] and indicate good chemical durability of melted and sintered composite materials. The corrosion rates were too low to allow for the detection of any uranium in the leaching solution.

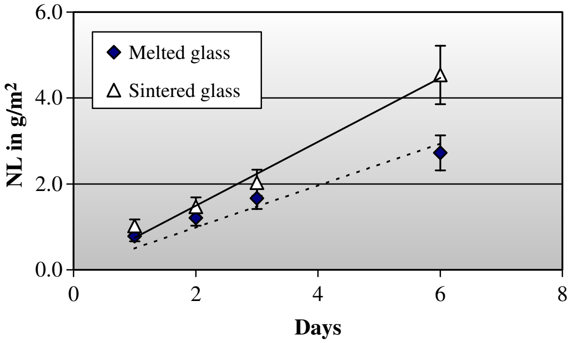

Fig. 10. Normalized mass loss of B for sintered and melted glass-TRISO-particles composite corroded at 90 °C in pure water with SA/V = 100 m^{-1}.

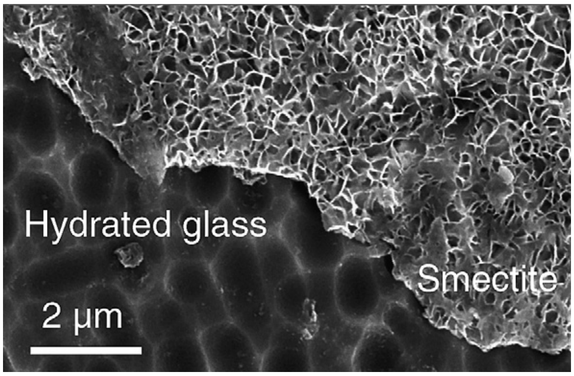

Fig. 11. SEM micrograph of corroded glass surface showing hydrated glass and a smectite-like phase.

The SEM examination of the leached glass surface shows dissolution pattern and a clay-like secondary phase formed after 8d of reaction (Fig. 11). EDS analysis of glass surface is given in Table 2. B and Li are not detected by EDS, which explains the sum of the oxides in the pristine glass of 77.3%. Compared to the pristine glass, the leached glass has lost silica and gained water, which is indicated by the decrease of the sum of oxides (73.6%). The clay-type phase has even lower silica content but high content of Zn. Similar phase was described by Crovisier et al. [20] and Abdelouas et al. [21] on the SON 68 French nuclear waste glass corroded in water at 250 °C. The authors identified the phase as a smectite. It is expected that the altered glass constitutes itself a confinement matrix for the coated particles. More work is necessary to identify its confinement properties with respect to corrosion of coated particles.

4. Summary and conclusions

The preliminary results described in this work show that confinement of TRISO-fuel particles in a glass matrix is possible. With the present data using an oxidizing melt process, immobilization of the particles in sintered glass appears to be more promising than in melted glass. Identified advantages of sintered glass are: (1) low processing temperature in air that better preserves the TRISO-particles, (2) good coating properties, (3) no heat treatment of TRISO-particles is required prior to vitrification and (4) good chemical durability. The quality of sintered glass can still be improved to reduce the porosity by optimizing the sintering time, processing temperature and perhaps sintering under pressure and at temperature. Vitrification by melting is possible but requires high processing temperatures

Table 2
EDS chemical compositions of pristine and corroded glass average of 10 analyses (wt%)

	SiO_2	Al_2O_3	Na_2O	CaO	ZnO	ZrO_2	Total (%)
Smectite	45.9 ± 1.5	5.3 ± 0.5	5.4 ± 0.5	4.2 ± 0.2	7.1 ± 0.7	2.8 ± 0.2	70.7
Hydrated glass	53.0 ± 2.4	4.2 ± 0.2	6.2 ± 0.4	4.8 ± 0.1	3.2 ± 0.7	2.2 ± 0.2	73.6
Pristine glass	55.8 ± 0.6	4.5 ± 0.2	6.0 ± 0.3	5.2 ± 0.2	3.3 ± 0.8	2.5 ± 0.3	77.3

of about 1150 °C in inert atmosphere conditions to prevent rapid oxidation of TRISO-coatings and ultimately fuel kernels. Oxidation of the particle coating may release volatile radionuclides including ^{14}C, ^{129}I, ^{134,135,137}Cs and maybe ^{36}Cl. In an industrial vitrification plant it is expected that Cs can easily be incorporated into the glass but this is much more difficult for ^{14}C and ^{129}I.

Though vitrification of irradiated TRISO-particles was not tested it is expected that the sintered glass remains stable under high radiation doses. In fact, this glass is being used as additive for high-level waste vitrification in France (R7T7 nuclear waste glass). The R7T7 glass holds an initial specific activity of alpha emitters of 1.7 TBq, a beta–gamma activity of 110 TBq and a thermal load of 13.5 W per liter of glass. If similar activity loading and heat production is envisioned for coated particle loaded glass this suggests that each liter of our sintered composite glass can be used to immobilize 2.7×10^5 TRISO-particles (UOX fuel, burnup 19% FIMA, initial enrichment 10%, 3 years of decay, H. Werner – personal communication) corresponding to volume fraction of coated particles of about 16% and an average distance between the surfaces of two particles of 0.8 mm. Nevertheless, tests with real active material and high load of TRISO particles are necessary to confirm this argumentation.

Acknowledgement

We would like to thank A. Barreau from the Institut des Matériaux de Nantes Jean Rouxel (France) for scanning electron microscopy studies.

References

[1] A.-W. Mehner, W. Heit, K. Röllig, H. Ragoss, H. Müller, J. Nucl. Mater. 124 (1984) 25.
[2] H. Nickel, H. Nabielek, G. Pott, A.W. Mehner, Nucl. Eng. Des. 217 (2002) 141.
[3] W. Shenk, A. Naoumidis, H. Nickel, J. Nucl. Mater. 171 (1990) 9.
[4] G.K. Miller, D.A. Petti, J.T. Makai, J. Nucl. Mater. 334 (2004) 79.
[5] R.E. Bullock, Carbon 19 (1981) 255.
[6] T. Ogawa, K. Fukuda, H. Sekino, M. Numata, K. Ikawa, J. Nucl. Mater. 135 (1985) 18.
[7] E. Proksch, A. Strigl, H. Nabielek, J. Nucl. Mater. 139 (1986) 83.
[8] M. Akabori, K. Fukuda, J. Nucl. Mater. 183 (1991) 70.
[9] K. Minato, T. Ogawa, K. Fukada, M. Shimizu, J. Nucl. Mater. 208 (1994) 266.
[10] M. Naghedolfeizi, J.-S. Chung, R. Morris, G.E. Ice, W.B. Yun, Z. Cai, B. Lai, J. Nucl. Mater. 312 (2003) 146.
[11] D.A. Petti, J. Buongiorno, J.T. Maki, R.R. Hobbins, G.K. Miller, Nucl. Eng. Des. 222 (2003) 281.
[12] G. Miller, D.A. Petti, D.J. Varacalle Jr., J.T. Maki, J. Nucl. Mater. 317 (2003) 69.
[13] W. Schenk, G. Pott, H. Nabielek, J. Nucl. Mater. 171 (1990) 19.
[14] W. Schenk, K. Verfondern, H. Nabielek, E.H. Toscano, Limits of LEU TRISO particle performance, in: Proceedings HTR-N, International HTR Fuel Seminar, Brussels, Belgium, February 1–2, 2001.
[15] K. Sawa, S. Ueta, Nucl. Eng. Des. 233 (2004) 163.
[16] E. Merz, H. Brücher, St. Halaszovich, in: K. Kugeler, H. Neis, G. Ballensiefen (Eds.), Fortschritte in der Energietechnik. Monographien des Forschungszentrums Jülich Bd 8, 1993, p. 336.
[17] R. Gieré, P. Stille, Energy, Waste and the Environment: A Geochemical Perspective, Geological Society of London, Special Publication 236, 2004, 688 pp. ISBN 1-86239-167-x.
[18] D. Rebiscoul, P. Frugier, S. Gin, A. Ayral, J. Nucl. Mater. 342 (2005) 26.
[19] I. Tovena, Influence de la composition des verres nucléaires sur leur altérabilité (Influene of nuclear waste glasses composition on their alterability), PhD Thesis, University of Montpellier II, France, 1995.
[20] J.-L. Crovisier, E. Vernaz, J.L. Dussossoy, J. Caurel, Appl. Clay Sci. 7 (1992) 47.
[21] A. Abdelouas, J.-L. Crovisier, J. Caurel, E. Vernaz, C.R. Acad. Sci. Paris 317 (1993) 1333.