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Fabrication of transmutation and incineration targets by infiltration of porous pellets by radioactive solutions

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Abstract

Infiltration of metal nitrate solutions into porous pellets, followed by thermal conversion of the nitrate to oxide and sintering of the pellets, provides an alternative procedure for the fabrication of targets for the transmutation and incineration of actinides and fission products. The infiltration rate of metal (Ce and Pu) nitrate solutions into porous spinel ($MgAl_2O_4$) pellets depends on the viscosity of the solution, while the infiltrant content depends on the solution concentration and the pellet porosity. The infiltration depth is proportional to the square root of the time the pellet is immersed in the solution. Tailored distributions of the infiltrant can be achieved either by selecting the immersion time, or by applying an impenetrable coating on selected regions of the pellet surface.

Keywords: Fabrication; Infiltration; Plutonium; Spinel; Transmutation

1. Introduction

Transmutation and incineration are innovative options in the management and disposal of fission products and actinides. In order to improve the efficiency of these processes, materials inert to neutron activation are being considered as alternatives to UO_2 as a support material, as the latter generates actinides during irradiation. These inert matrices are selected on the basis of their thermal conductivity, melting point, compatibility with the reactor coolant and their resistance to damage by neutrons, fission products and α-decay. Spinel ($MgAl_2O_4$) is one material which meets these criteria.

The fabrication of targets for transmutation and incineration of actinides and fission products will require a reconsideration of conventional processes and the development of new procedures compatible with the high activity of these materials. In particular, fabrication processes should be suitable for remote handling and extensive automation so that they are compatible with the necessarily more stringent radiation protection measures. Furthermore, dust generation should be low and waste minimal. Infiltration of a liquid into a solid porous preformed material [1–5] is a process which complies with these requirements and has already been used for the fabrication of spinel targets containing 10% Am [6], which are now under irradiation in HFR, Petten [7].

Infiltration of a liquid into a porous preform can be described by the Washburn model [8], which considers the porous medium as a constant cross section capillary. In this model, the depth (d) to which an infiltrant penetrates the porous preform is given by

$$d = \left(\frac{\gamma r t \cos \theta}{2\eta} \right)^{1/2} \tag{1}$$

where γ is the surface energy, θ the contact angle between the infiltrant and the solid, η the infiltrant viscosity, r the pore radius and t the time during which infiltration has occurred. If it is assumed that all terms except d and t remain constant during the infiltration period, the infiltration depth should be proportional to $t^{1/2}$. This paper presents kinetic measurements of the infiltration of porous spinel pellets by cerium and plutonium nitrate solutions, and the distribution and microstructure of the infiltrant within the pellet after its conversion to oxide. A method to obtain a particular tailored distribution of the infiltrant throughout the pellet is also demonstrated.

2. Experimental procedure

2.1. Preparation of green pellets

Spinel powder (Baikalox S33CR, Baikowski Chemie) was granulated and pressed into pellets (470 MPa) in a 6.6 mm diameter cylindrical die. The lubricant (zinc stear-

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ate) was removed by pyrolysis by firing the pellets at 650°C for 2 h. The green pellets prepared using this method had densities between 50 and 53% of the theoretical density (3600 kg m^{-3}). Following sintering at 1640°C for 8 h in an Ar/H_2 atmosphere, their density increased to 94–95% of the theoretical value.

2.2. Infiltration procedure

Infiltration of sets of pellets with the same (±0.3%) porosity was achieved by their complete immersion, for the required time (5–600 s), in the appropriate nitrate (cerium or plutonium) solution at room temperature. After their removal from solution, the pellets were dried for 90 min at 100°C to eliminate excess water. Thermal decomposition and conversion of the infiltrated nitrate to oxide was achieved by heating in air at 800°C, after which the pellets were sintered at 1640°C in an Ar/H_2 atmosphere for 8 h.

2.3. Characterisation

The metal content, defined as the weight of metal to the total weight of the sample, was determined from the weight gain following sintering, assuming an O/Pu or O/Ce ratio of 2.0. Qualitative information on the macroscopic distribution of cerium or plutonium within the pellets was obtained using X-ray radiography. In the case of plutonium, the infiltrant distribution was also determined by α-autoradiography from the polished surfaces of sectioned pellets. Microstructural examination was performed using optical microscopy and scanning electron microscopy (SEM).

3. Results and discussion

The infiltration depth following immersion of the pellet in the metal nitrate solution for a given time can be calculated, in principle at least, from Eq. (1). As the variables relating to the infiltrant liquid (θ,γ,η) are unknown, however, the infiltration depth (d) can be calculated more conveniently from the fractional weight gain (FWG) of the porous spinel pellet after infiltration of the solution. If it is assumed that the pellet is infiltrated uniformly from all sides, and that the concentration of the second phase throughout the infiltrated region is constant, the fractional weight gain is given by [1]

$$\mathrm{FWG} = \frac{\rho_i}{\rho_o}\frac{P}{1-P}F\left[1-\left(1-\frac{d}{r}\right)^2\left(1-\frac{2d}{h}\right)\right] \qquad (2)$$

where ρ_i is the density of the infiltrant solution, ρ_o the theoretical density of the matrix material, P the pellet porosity, F the degree of filling of the pores, and r and h the pellet radius and height, respectively.

Assuming F is unity, the infiltration depth has been calculated following immersion of the pellets in various solutions for given times. The results, presented in Fig. 1, exhibit two distinct regimes. In the first, rapid infiltration occurs due to the flow of the solution into the porous pellets. As the liquid enters the pellet, the internal pressure of the trapped gas increases and eventually counteracts the capillary forces driving the infiltration. In this second regime, the infiltration rate decreases and is determined by the flow of the trapped air through the liquid infiltrant to the surface of the pellet, where it forms bubbles and is eventually released into the solution itself. In this second region the Washburn model as given in Eq. (1) is no longer applicable.

At lower Pu and Ce concentrations, the infiltration rate in the initial regime is highest (see Table 1). This is most likely due to the lower viscosity of these solutions. Indeed, in this initial regime the infiltration rate is inversely proportional to the viscosity, as expected from the simple Washburn model. The measurements (see Table 1) also

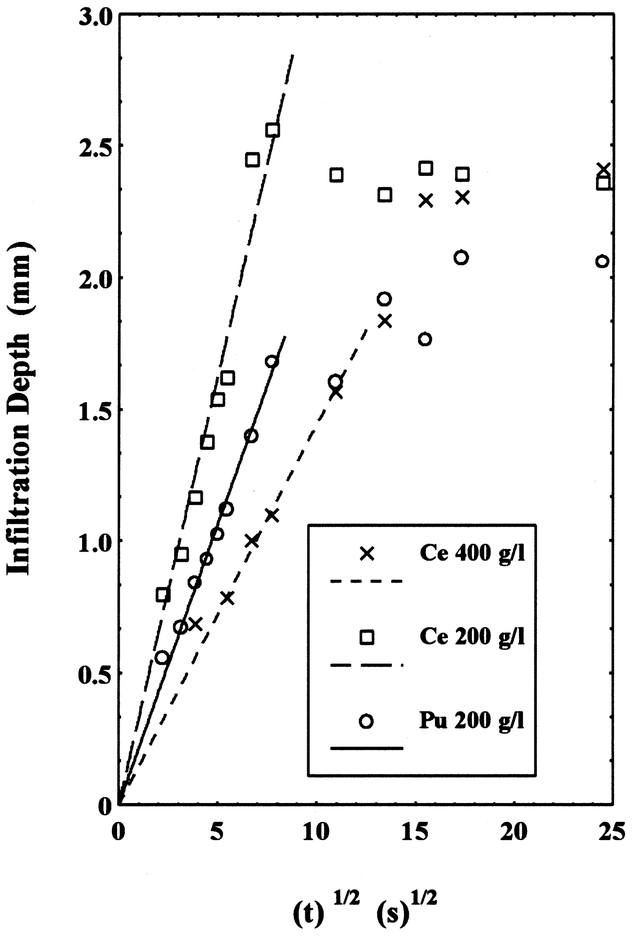

Fig. 1. Infiltration depth, calculated from the weight of liquid infiltrated, as a function of $(\mathrm{time})^{1/2}$ for the infiltration of Pu and Ce nitrate solutions into porous spinel pellets.

Table 1
Infiltration of spinel pellets by metal nitrate solutions

Metal	Concentration of metal ($g\,l^{-1}$)	Solution viscosity, ν (cPs)	Infiltration constant ($mm^2\,s^{-1}$)	Pellet porosity[a] (%)	Metal infiltrated[b] (%)
Ce	200	2	0.11	48.4±0.4	4.2
	400	10	0.02	50.1±0.1	8.6
Pu	200		0.05	47.6±0.2	4.4

[a] Prior to infiltration.
[b] Following immersion in the solution for 600 s.

show that the weight of infiltrated metal, following infiltration for 600 s, is roughly proportional to its concentration in the original metal nitrate solution.

X-ray radiographs of pellets infiltrated for given times are shown in Fig. 2. These measurements show a dark region in the form of a shell, containing Ce or Pu, near the pellet surface. The lighter central region of the radiograph defines the region not reached by the infiltrant. The thickness of the Pu or Ce containing shell (i.e. the infiltration depth) increases with infiltration time, as expected. Even at the longest immersion times, however, the infiltrant does not reach the central region of the pellet. Complete infiltration of the pellet can be achieved by providing an escape route for the gas within the pellet [4,6].

A pellet infiltrated with a Pu solution for 30 s was sectioned axially and polished, and α-autoradiographs, resulting from Pu decay, measured (see Fig. 3). The Pu is found exclusively in a shell extending about 1.4 mm into the pellet, which is consistent with the X-ray radiography measurement of the same sample. The infiltration depths determined from the fractional weight gain (see Eq. (2)) are always lower than those determined from X-ray radiography. This could be due to incomplete filling of the pores during infiltration. Indeed, the degree of pore filling can be calculated from the depth determined from X-ray radiography and $F = 0.97 \pm 0.02$ is obtained.

Optical micrographs of the polished surfaces of sectioned pellets show that the Pu is found in particles with diameters less than 3 μm (see Fig. 4) which are distributed throughout the infiltrated region. SEM measurements have been made on spinel pellets infiltrated with Ce (see Fig. 5) and the Ce is found in distinct particles with diameters less than 2 μm. Similar results were also found in samples prepared by infiltration of spinel pellets by Am solutions [6].

These investigations have shown that the infiltrant can be preferentially incorporated in the surface regions of the pellet if they are completely immersed, for short periods, in the solution. Further tailoring of the infiltrant distribution can be achieved by preventing infiltration through specific surfaces of the pellet. Fig. 6 shows the X-ray radiographs of spinel pellets whose ends were sealed with a low melting point hydrocarbon prior to their immersion in a Ce solution. The central axial region contains no

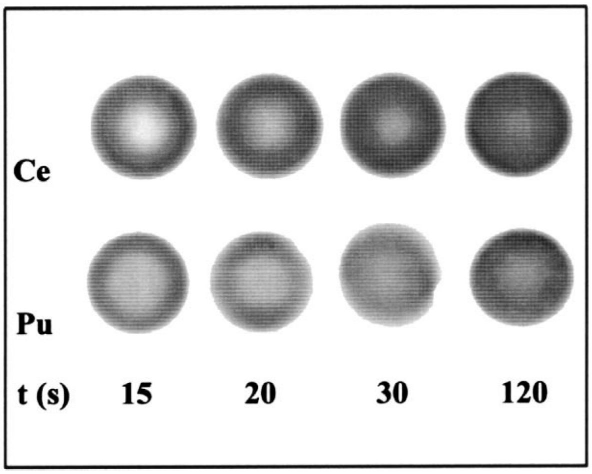

Fig. 2. Axial X-ray radiographs of pellets infiltrated with Ce and Pu nitrate ($200\,g\,l^{-1}$) solutions. The immersion time is indicated.

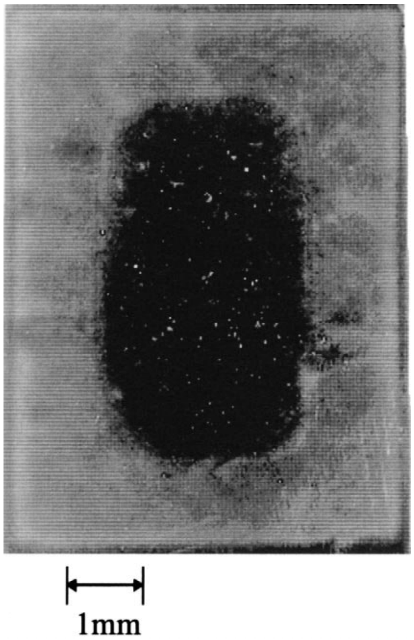

Fig. 3. α-Autoradiograph taken from the polished surface of a sectioned spinel pellet following infiltration of a plutonium nitrate solution for 30 s.

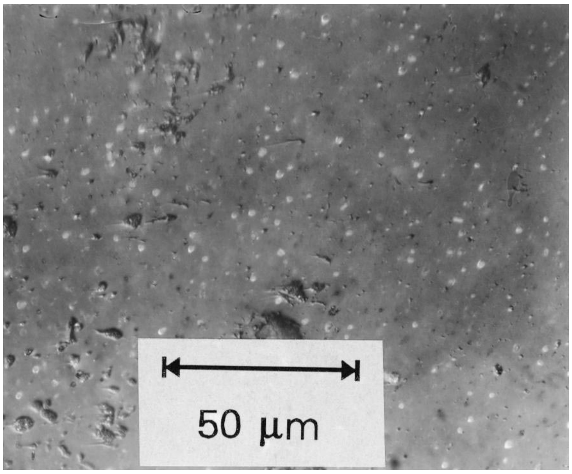

Fig. 4. Optical micrograph of a spinel sample following infiltration of Pu. The Pu containing particles (white) have diameters less than 2–3 µm.

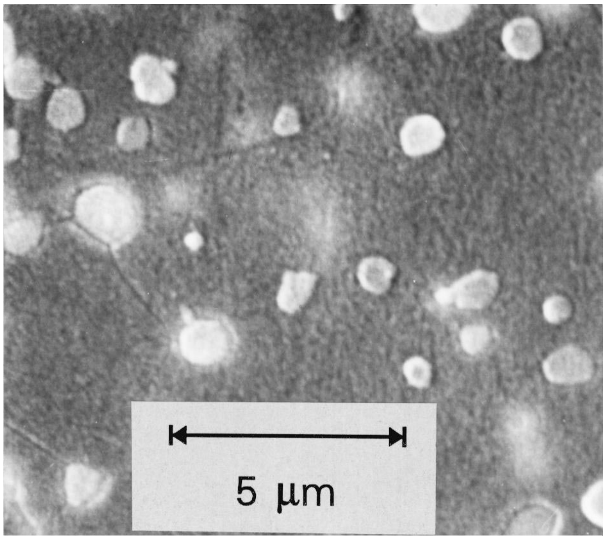

Fig. 5. SEM of a spinel sample following infiltration of Ce. The Ce containing particles have diameters less than 2 µm.

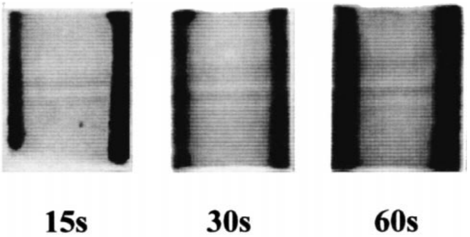

Fig. 6. Radial X-radiographs of pellets infiltrated with Ce solutions (400 g l^{-1}) for various times. The ends of the pellets were sealed prior to their immersion in the solution.

infiltrant. Pellets produced in this way have the advantage that the heat produced by fissioning an actinide infiltrant is only present at the surface and can be readily transported. Annular pellets offer a similar solution [9], but their mechanical stability is lower.

4. Conclusions

This work has demonstrated that infiltration is an effective technique for introducing an additional phase into a porous material. The content of the second phase can be controlled by a combination of the liquid precursor properties and the infiltration time. Within a region where the simple Washburn model applies, the depth reached by the infiltrant is proportional to the square root of the immersion time. Radiography measurements show that the distribution of Ce or Pu is relatively uniform throughout the infiltrated region. The distribution of the infiltrant within the pellet can be tailored by adjusting the infiltration time and/or by inhibiting infiltration through certain regions of the pellet surface.

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