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Highly porous yttrium aluminium garnet (YAG) particles synthesised by a gel supported precipitation (GSP) process

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Yttrium aluminium garnet (YAG) has been successfully manufactured by a liquid to particle conversion process, usually known as the gel supported precipitation (GSP) method. The conversion involves a localised ammonia precipitation, which was successfully achieved without loss of stoichiometry, with respect to yttrium and aluminium, in the precipitation step. The resulting particles are in the form of near spherical beads, whose compaction behaviour exhibits a marked dependence on the Yttrium and Aluminium concentration in the feed solution. The pellet densities of ca. 90% of the theoretical density are ideal for minor actinide transmutation targets, where release of He produced by their irradiation in a nuclear reactor is necessary. Furthermore, the YAG particles produced by the GSP route are sufficiently porous, to enable their infiltration by an actinide nitrate solution. Tests using cerium nitrate solutions to simulate the minor actinide solutions have shown that up to 65 wt% of CeO_2 can be incorporated in YAG using this novel fabrication route.

1. Introduction

Yttrium aluminium garnet (YAG or $Al_5Y_3O_{12}$) is of great interest as a high temperature engineering material, due to its high temperature strength coupled with low creep rates [1]. Also some of its properties render it of interest for nuclear waste management applications. In particular, its relatively high melting point (2243 K) and the neutronic inertness of its constituent atoms have lead to its consideration as a matrix, into which minor actinides can be incorporated, and subsequently transmuted by neutron irradiation.

The fabrication of YAG has been investigated extensively. Single crystal YAG is expensive to produce [2], and a number of powder processing routes have been investigated for the production of high density material. The classical synthesis of YAG powders consists of the reaction of alumina and yttria powders at high temperatures. Under these conditions, however, control of microstructure and grain size is difficult and, due to the long exposure times required at these temperatures, the powders have to be milled, before being processed further. Wet chemical synthesis eliminates this disadvantage, and various alternatives have been tested. These include precipitation [3–6], sol gel methods starting from metal alkoxides [7] or ionic salt solutions [8–11], and also solution combustion [12, 13].

In these investigations, the final goal is the production of a composite material suitable for the incorporation of minor actinides (e.g., Am, Np) in oxide form for their transmutation and incineration in nuclear reactors. This is an innovative process being investigated for the minimisation of long-lived nuclear waste [14]. In contrast to optical applications, a high density product is not required. Rather lower densities {85–90% of the theoretical density (TD)} are preferable to allow the release helium (a by-product due to α decay in the actinide transmutation process) from the matrix and so avoid unacceptable swelling of the material [15]. If the density is too high, this helium can cause unacceptable material swelling. In addition, minor actinides have high radiotoxicity, so that simplified fabrication processes are a prerequisite for their handling. This paper describes details of a procedure based on the gel supported precipitation (GSP) method to synthesise YAG in the form of highly porous (near) spherical particles, into which the required metal can be infiltrated and further processed into pellets for irradiation. The influence of various process parameters on the morphology of the porous particles, and their compaction into pellets and sintering properties have been investigated.

2. Powder preparation and characterisation

Synthesis of pure YAG ($Y_3Al_5O_{12}$) was performed by the gel supported precipitation (GSP) method (see Fig. 1). Aqueous solutions of $Y(NO_3)_3 \cdot 6H_2O$ (Alfa 99.9% REACTON) and $Al(NO_3)_3 \cdot 9H_2O$ (Alfa 99.999% PURATRONIC) were mixed in a Y:Al molar ration of 3:5. (The corresponding chloride salts

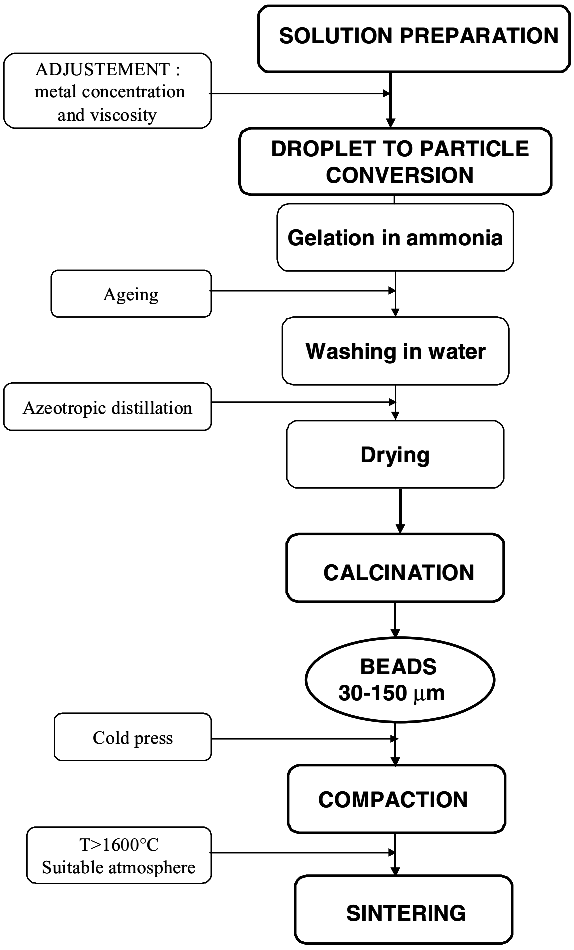

Figure 1 Flow diagram of the gel supported precipitation (GSP) process.

were also used as precursors in order to investigate the influence of the starting anions on the final product). Clear transparent solutions were obtained. The viscosity of this solution was adjusted by addition of a high viscosity organic polymer (Methocel, Dow Chemical). This feed solution was then dispersed using a rotating cup atomiser into droplets [16], which were collected in an ammonia bath where gelation occurred and the droplets were converted into solid gelled particles. The optimum precipitation pH of the ammonia bath has been discussed elsewhere [16, 17]. Aluminium hydroxide precipitates completely at pH = 6.5–7.5 but starts to redissolve in the presence of excess ammonia. Precipitation of yttrium hydroxide from an aqueous solution occurs at a pH close to 10. In this work, pH = 9.5 and pH = 10 were both tested successfully.

Aging of the gel particles in ammonia for 30 min was necessary to complete their gelation. Thereafter, the gelled material was washed several times with distilled water to remove residual ammonia and ammonium nitrate, whose presence can produce fractures during thermal treatment. Drying of the gelled particles was carried out by azeotropic distillation with tetrachloroethylene and was followed by a calcination step to pyrolyse any organics remaining in the structure and to form crystalline YAG from the gel hydroxides. Thermal gravimetric and differential thermal analyses (TG/DTA) were used to find a first indicator of the required calcination temperature. The results are shown in Fig. 2. The sample weight decreased significantly due to (a) the pyrolysis of the polymers present in the feed solution and (b) the conversion of aluminium and yttrium hydroxide into amorphous oxides. These processes were completed by about 700°C. The DTA curve shows an exothermic peak at 943°C, which is attributed to the crystallisation of YAG [18]. Indeed, X-ray diffraction (XRD) measurements of the uncalcined material found no evidence of crystallinity, whereas material heated to 1200°C (see Fig. 3) exhibited well defined peaks in XRD identical to those of stoichiometric YAG [19]. No additional peaks due to either Al_2O_3 or Y_2O_3 were identified indicating that, at least within the detection limits of XRD, the stoichiometry of the feed solution was maintained through the precipitation step. From the XRD data a lattice parameter of 1.2011 nm was determined, which compares well with literature values (1.20089 nm [19]).

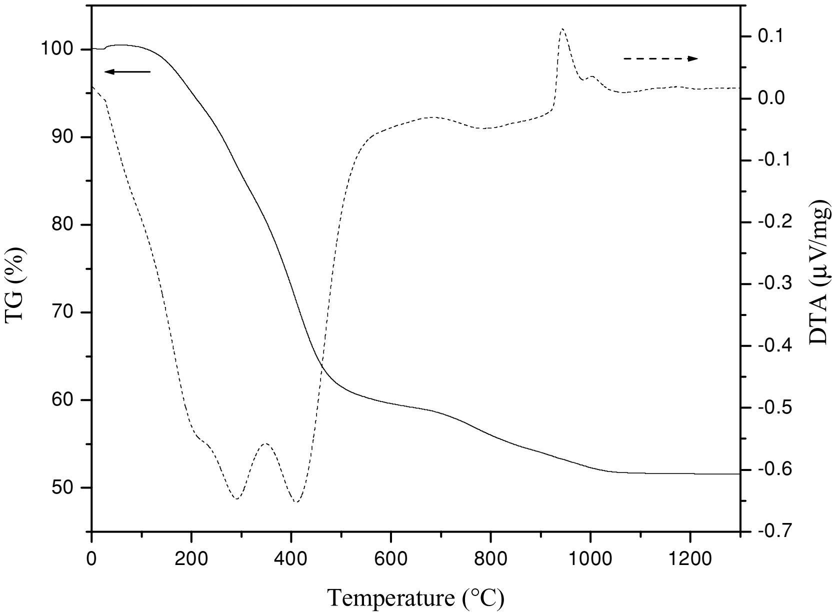

Figure 2 TGA and DTA measurements of YAG particles produced by the GSP method.

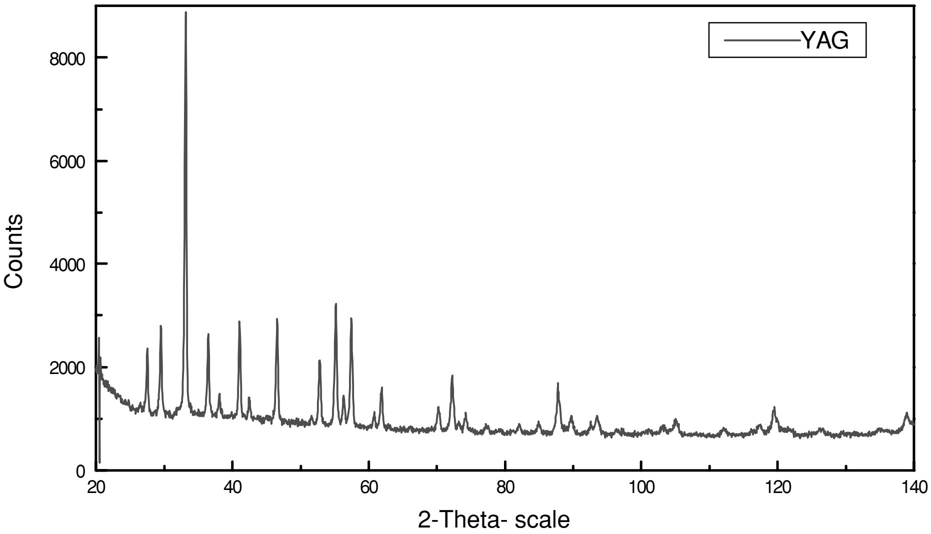

Figure 3 XRD of YAG beads after calcination at 1200°C.

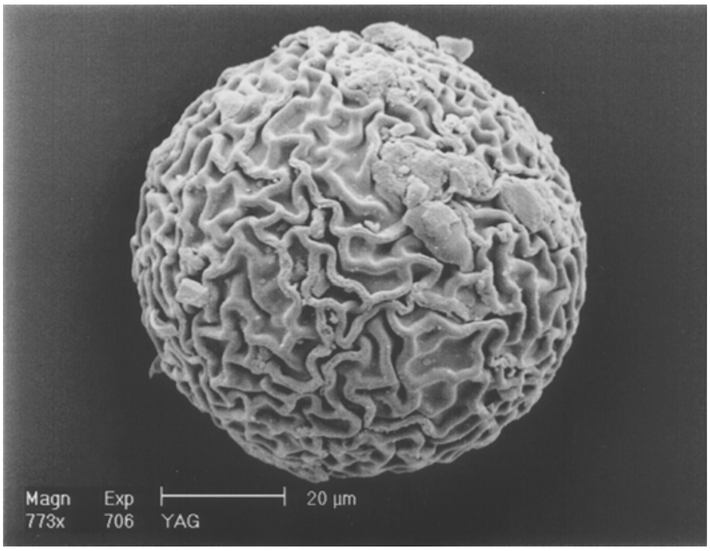

Figure 4 Scanning micrograph of a YAG particle after calcination at 850°C.

Fig. 4 shows an electron micrograph of a YAG particle after calcination. The rough surface is a first indicator of the high porosity of the beads. EDAX measurements of the Y/Al ratio at the particle were made at three random positions and the values 0.60, 0.58, and 0.62 corroborate the XRD data and indicate that the Y:Al ratio was maintained in the liquid to droplet conversion step.

3. Pelletisation of YAG powders

The calcined particles were compacted in a biaxial press at 390 MPa to form cylindrical pellets. Zinc stearate was used as lubricant. The relative density of the green pellets was 40–45% of the theoretical density. These green pellets were sintered in Ar/H_2 at a constant heating rate of 200°C/min between room temperature and 1650°C and were held at the latter temperature for 8 h. Pellet densities were calculated from measurements of their dimensions and weight, and are referenced to YAG theoretical density ($4.55\ g \cdot cm^{-3}$ [20]).

The concentration of the metal ions in the GSP feed solution has a significant influence on the compaction of particles and densification of the pellets manufactured by this processing route. The data in Fig. 5 shows the density and height (for a constant fill height of the press die) of the sintered YAG pellets obtained from particles produced from the chloride precursor solution. Similar results were obtained for nitrate precursors. The height and density of the final pellets depend markedly on the metal concentration in the feed solution. The final density increases with metal concentration, with a maximum density of only 87% TD being reached at highest initial metal concentrations. In contrast, the height of the pellets decreases with increasing metal concentration in the feed solution. As the fill height of the press was constant throughout, the reduction in pellet height predominantly reflects the decrease in the tap density of the YAG beads. A ceramograph of a sectioned and polished YAG pellet is shown in Fig. 6. The pellets are devoid of cracks and exhibit a uniform distribution of the porosity throughout. No memory effect of the original bead form is found, indicating that sintering

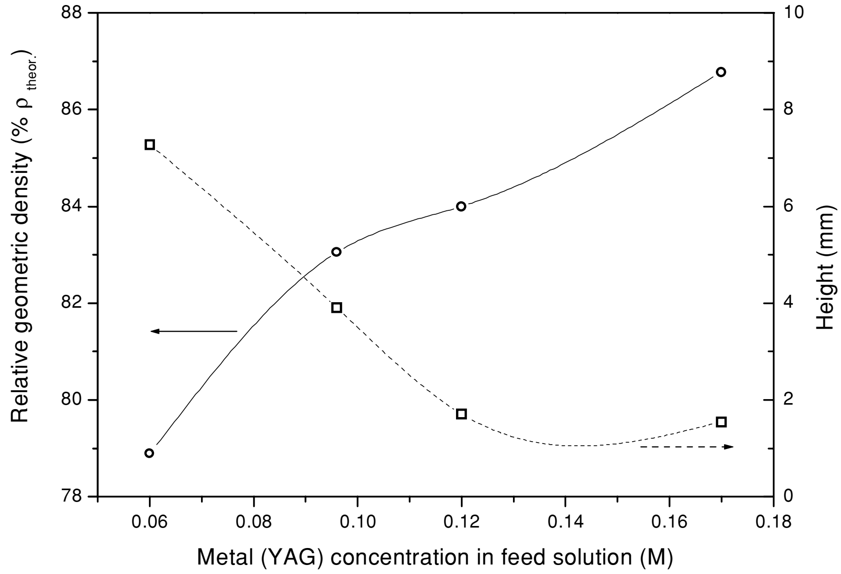

Figure 5 Density and height of pellets fabricated from YAG beads as a function of the initial metal content in the process feed solution.

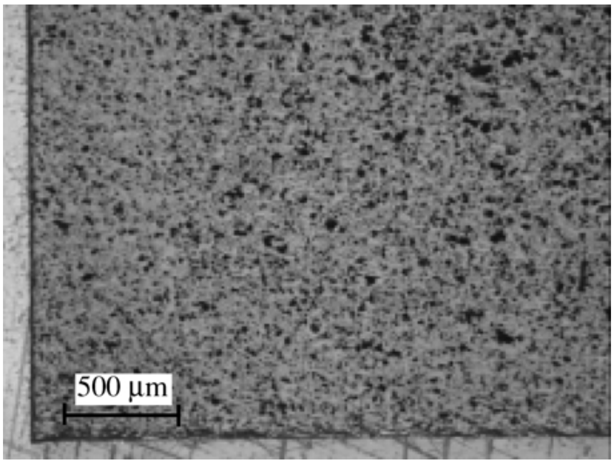

Figure 6 Ceramograph of a sectioned and polished YAG pellet.

between individual precursor beads spheres was effective. As mentioned earlier, porosity and especially open porosity is a prerequisite for transmutation targets, in order to permit He release from the target.

4. YAG beads: application to minor actinide fabrication

As discussed above, the fabrication of minor actinides requires considerable process simplification to minimise and automate the production steps that require extensive operator shielding. Here the high porosity of the calcined YAG beads produced by the GSP method can play an important role [21]. A nitrate solution of the actinide can be readily prepared and infiltrated into the porous beads. The infiltration is terminated when the incipient wetness point is reached, i.e., the point at which the interstitial volume between the beads is filled with liquid, and the solid mass becomes fluid. Following a calcination step to convert the actinide nitrate solution in the beads to oxide, pellets can be pressed as above.

Process parameter investigations on the infiltration of YAG beads have been made using cerium nitrate solutions to simulate the actinide. The results in Fig. 7 show the quantity of solution (normalised to a unitary mass of YAG) added to the beads in order to reach the incipient wetness point as a function of the preparation condition of the beads (metal concentration in the feed solution). As the metal concentration in the feed solution used for the bead fabrication is increased the bead porosity also increases and more solution can be infiltrated. This effect is in accord with the tap density behaviour as noted in the pressing of the beads.

The quantity of CeO_2 that can be infiltrated increases with the concentration of Ce in the infiltration solution (see Fig. 8). A linear dependence between the Ce infiltrated and the nitrate solution concentration is observed, but does not pass through the origin. This could be an artefact due to the viscosity, η of the feed solution, which increases from 2 to 10 cPs for 200 and 400 g/l solutions. When a liquid infiltrates a porous solid, the penetration depth at any given time is, according to the Washburn model [22], proportional to $\eta^{-1/2}$. Even though the physical dimensions of the beads are

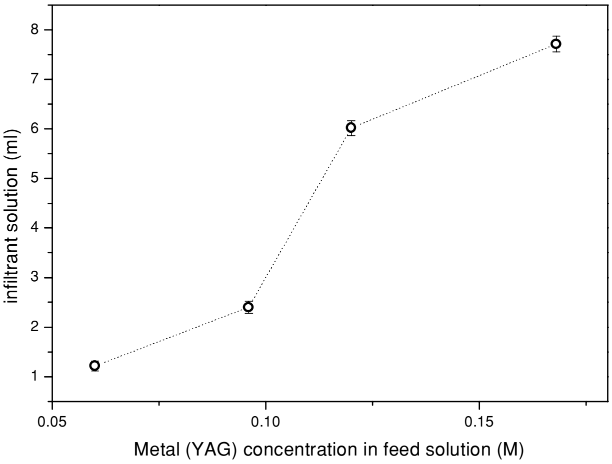

Figure 7 Volume of infiltrant solution (normalised to the unitary YAG mass) infiltrated as a function of the initial concentration of the feed solution.

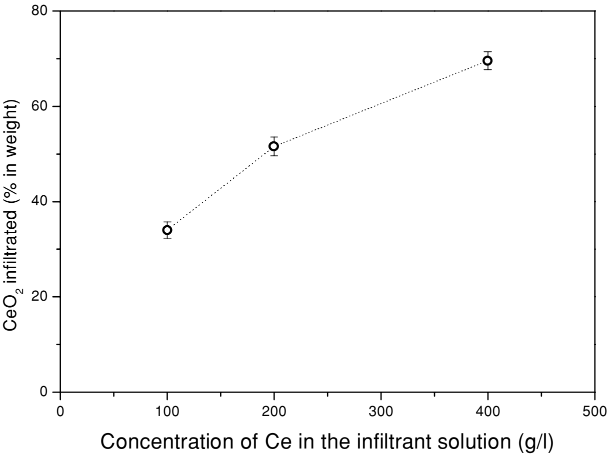

Figure 8 Mass% of CeO_2 infiltrated as a function of the Ce content in the Ce nitrate infiltration solution.

relatively small, a reduced infiltration rate with more viscous (i.e., concentrated) Ce solutions leads to the observation of the incipient wetness point, prior to complete infiltration of the beads. In addition, the higher viscosity liquid also increases the barrier to diffusion and release of air trapped in the internal bead structure. Nevertheless, these results show that the YAG beads produced by the GSP method are extremely well suited to the infiltration process and significant quantities (60% weight) of metal oxides can be incorporated so that the production of targets containing minor actinides for actinide transmutation is feasible using this route.

5. Conclusions

YAG has been successfully manufactured by the gel supported precipitation (GSP) method. The high porosity of the YAG beads renders them ideal for infiltration of actinide nitrate solutions for the production of transmutation targets. The product pellets with a final density of 85–90% TD are well suited to applications where YAG is used as a matrix for transmuting minor actinides. He produced in the transmutation process can be released via the open porosity to the fuel pin plenum and swelling of the material itself is thus avoided. Further process development (e.g., compaction-granulation and milling) can be envisaged if higher density materials are required for optical applications [23].

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