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Journal of Nuclear Materials 354 (2006) 137–142

journal of nuclear materials

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Synthesis and sintering studies on Dy_2TiO_5 prepared by polymer carrier chemical process

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Received 28 January 2005; accepted 28 March 2006

Abstract

Dysprosium monotitanate (Dy_2TiO_5) powders were successfully synthesized by a polymer carrier chemical process using ethylene glycol as an organic carrier for the metal cations. The synthesis behavior of the powders was investigated by thermal analysis and X-ray diffraction methods. The microstructures of the synthesized powder and sintered pellets were also investigated using scanning electron microscopy. The ethylene glycol process was shown to be a practically viable process to prepare a submicron-sized and highly sinterable Dy_2TiO_5 powders.

1. Introduction

Cadmium, boron and hafnium and their compounds with large absorption cross-sections have been used as control rod materials. Boron (in the form of B_4C) is generally used in fast breeder reactors, however, accumulates large radiation induced damages caused by B [*n*, α] Li reactions on ^{10}B, the formation of He bubbles nucleates swelling and cracks and thereby reduces the lifetime of control rods [1]. Among the lanthanides, dysprosium and gadolinium have relatively large thermal neutron absorption cross-sections, and dysprosium monotitanate (Dy_2TiO_5) is an attractive control rod material as powder (density of 4–5 g/cm^3) or pellets (density of 6 g/cm^3 and more) for thermal neutron reactors [2]. The main advantages are the high neutron absorption cross-section, lower swelling and stable under neutron irradiation, moreover, high melting points, good mechanical properties and thermo-chemical stability with the cladding and ease of fabrication [3].

Generally, dysprosium titanate has been prepared by direct mixing of the two oxides followed by calcinations, compaction and sintering [2]. Meanwhile, chemically derived ceramic powders have excellent properties such as high purity, submicron size, high reactivity, and homogeneity on a molecular scale, however, they are expensive to produce and the throughput is low [4,5]. A better inexpensive

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doi:10.1016/j.jnucmat.2006.03.013

polymer, polyvinyl alcohol (PVA), was used as the organic carrier instead of the Pechini resin. The PVA polymer, which is a non-chelating polymer having large chain molecules as the polymeric carrier, has hydroxyl functional groups [6,7]. A steric entrapment of the metal ions was achieved using these large chain molecules, and finally soft and bulky ceramic precursors can be obtained, however, the PVA polymer only works with systems that are water soluble. By applying another polymer, ethylene glycol (EG) polymerizing agent, the process can be extended to chemicals that decompose in water, such as titanium isopropoxide. In particular, ethylene glycol can act as an effective solvent for wet chemical synthesis of titanate powder because a water-soluble titanium salt is not available commercially [8].

In this study, the authors have carried out a novel powder synthesis process using a simple-structured and an inexpensive polymer, ethylene glycol (EG), as the organic carrier for the preparation of Dy_2TiO_5 powder. The synthesis of the powder is reduced to a few simple steps rather than complex procedures such as in sol–gel. Additionally, the sintering behavior of the Dy_2TiO_5 pellets is investigated in a comparison with the pellets prepared by the solid-state synthesis method.

2. Experimental procedure

Titanium (IV) isopropoxide (TISO, $Ti(OC_3H_7)_4$, RG, Alfa Aesar Chem) and dysprosium nitrate pentahydrate ($Dy(NO_3)_3 \cdot 5H_2O$, RG, Aldrich Chem) were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chemical, FW:62.07). The transparent solution was then allowed to gel for 48 h in a drying oven at 80 °C. The dried gels were then calcined at various temperatures. Finally, the calcined powders were ball-milled to break up an agglomeration with zirconia media for 6 h. The ball-milled powder was compacted by pressing under 30 MPa and sintered in an air atmosphere at various temperatures.

Dy_2TiO_5 was also prepared by the standard solid-state synthesis route (hereafter called SS). Stoichiometric amounts of dysprosium and titanium oxide powders were mixed with zirconia ball media for about 5 h in alcohol. The homogeneous powder mix was calcined at 1300 °C for 20 h and compacted by pressing and then cold isostatic pressed (CIPed) at a pressure of 200 MPa using a uniaxial hydraulic pressing. Fig. 1(a) and (b) show the details of the preparation process. DTA/TG analysis and XRD, SEM were used to characterize the physical and chemical properties.

3. Results and discussion

3.1. Characterization of the powder

In the synthesis of dysprosium monotitanate, precipitates were formed in the solution of the ethylene glycol containing TISO, due to the water contained in the solution but they were dissolved after stirring [9]. After drying, the mixed solution became very viscous and a gel resulted. The gel is probably due to the cross-linking of the EG and TISO. Application of heating to the gel resulted in a charred foam structure.

Simultaneous DTA/TG results of the powder precursor gel from room temperature to 1200 °C are given in Fig. 2. Exothermic reactions were observed at 107 °C, 160–360 °C and about 400 °C. The temperature range of decomposition, which is indicated by the weight loss, was 70–400 °C. Beyond 400 °C, the percent of decomposition was less than 3%. The initial weight loss (70–150 °C) was due to a condensation of the precursor gel in the drying condition. This was followed by the release of nitrates. Pyrolysis of NO_x gases from nitrate source and of polymer chain from EG were observed in the temperature range of 150–360 °C. These decompositions were accompanied with the exothermic reaction at 160–360 °C. In sequence, an oxidation of the carbon from the pyrolysed organics occurred at 360–410 °C with the large exothermic peak. The continuous weight loss after 400 °C in a small portion may be due to a burn-out of the residual carbon caused by the fast heating rate. After 900 °C, any weight loss was not detected.

The phases at the different calcined temperatures were identified by the XRD technique (see in Fig. 3). The powder samples were calcined for 1 h at each temperature. A crystalline phase was observed at 800 °C, while an amorphous phase was detected below 800 °C. The orthorhombic phase, the low temperature phase, of dysprosium titanate was observed for precursor powder calcined up to 1300 °C for 1 h. With a calcination temperature increase, the transformation from orthorhombic to hexagonal phase occurred at 1300 °C, and complete conversion to the hexagonal phase was observed at 1400 °C for 1 h [2,3,10,11]. Different crystal

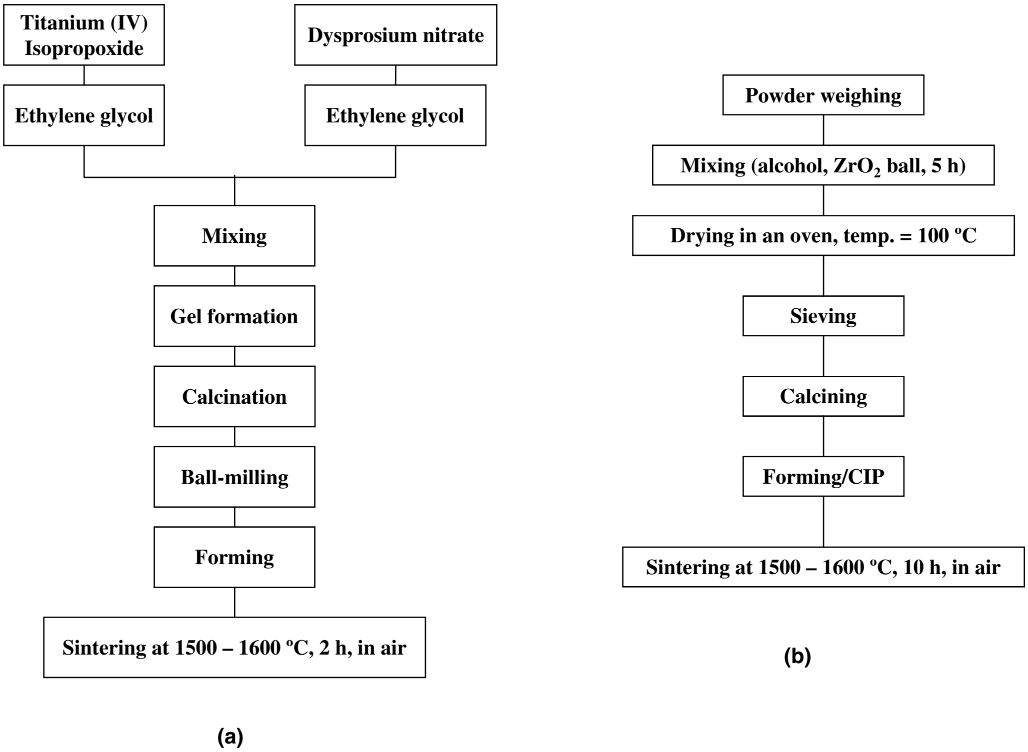

Fig. 1. Flow charts for the synthesis of Dy_2TiO_5 powder (a) EG process and (b) SS process.

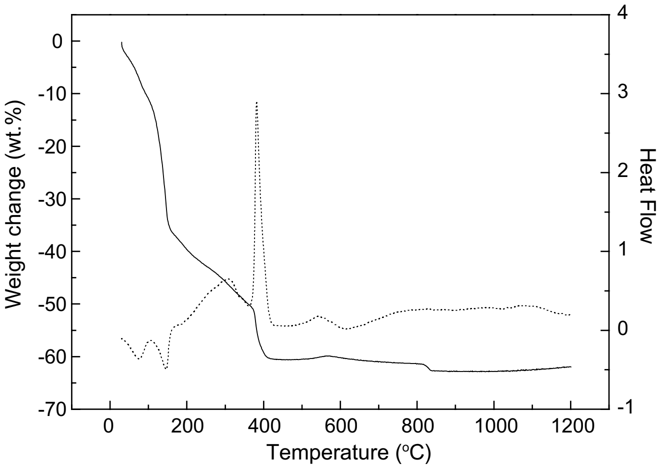

Fig. 2. DTA/TGA curves of the Dy_2TiO_5 precursor gel made by EG process.

structures of dysprosium titanate can be obtained by changing the calcination temperature.

The powder morphology of the crystalline at 900 °C and ball-milled powder prepared by EG method are shown in Fig. 4. The soft and porous agglomerated powder was ground easily by the simple milling process. In the SEM micrograph of the ball-milled powder, significantly reduced particles to submicron in size were observed. The specific surface areas and particle size of the calcined Dy_2TiO_5 powders are listed in Table 1. The calcined powder prepared by EG had a high specific surface area of 14.0 m^2/g and submicron-sized crystalline particles of 0.38 μm in a comparison with the SS cases.

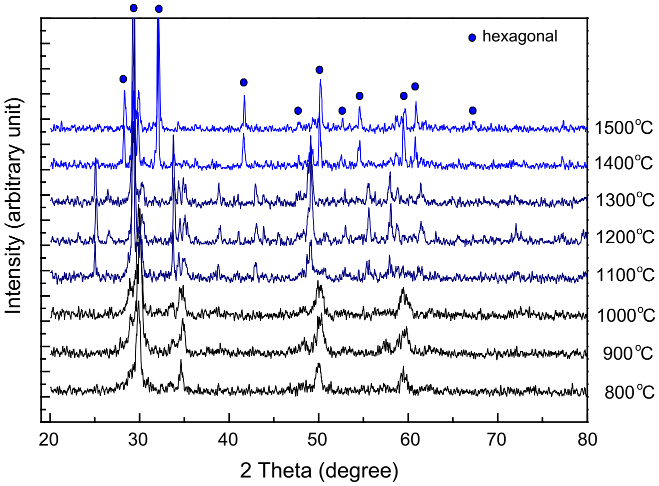

Fig. 3. XRD patterns of Dy_2TiO_5 powder at various temperatures.

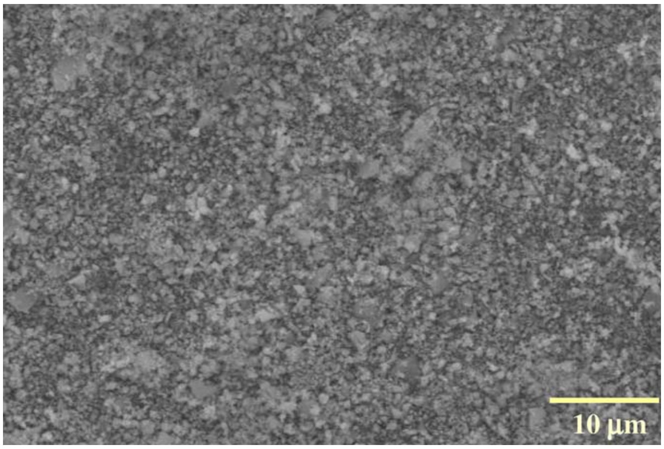

Fig. 4. SEM micrograph of Dy_2TiO_5 powder calcined at 900 °C for 1 h and ball milled.

Table 1
Specific surface areas and particle size of Dy_2TiO_5 powders

Process	Specific surface area (m^2/g)	Particle size (μm)
EG	14.0	0.38
SS	3.5	1.52

3.2. Sintering behavior

In order to investigate the sintering behavior of the powder compacts prepared by the EG and SS processes, the compacts were sintered at various temperatures with different holding time. The measured green density of cold isostatic-pressed powder compact prepared by the SS process was 60% of theoretical density. The microstructures of Dy_2TiO_5 samples sintered for 2 h by the EG process and 10 h by the SS process at 1500 °C and 1600 °C are shown in Fig. 5, respectively. The SS sample sintered at 1500 °C (see in Fig. 5(a)) contained continuous pore channels (density = 6.21 g/cm^3, 85% TD [13]) and it showed large irregular grains. At 1600 °C (see in Fig. 5(c)), the sample of SS process showed a rapid grain coarsening and it resulted in large and irregular shaped pore entrapments on the intra and inter grains. In the case of the samples of the EG process (see in Fig. 5 (b) and (d), density = 6.93 g/cm^3, 95% TD at 1500 °C), however, uniform and small-sized pores were located on the grain boundary. Fig. 6 shows the polished and etched surfaces of the pellets. The EG sample sintered at 1600 °C (see in Fig. 6(b), density = 7.04 g/cm^3, 96% TD) exhibited

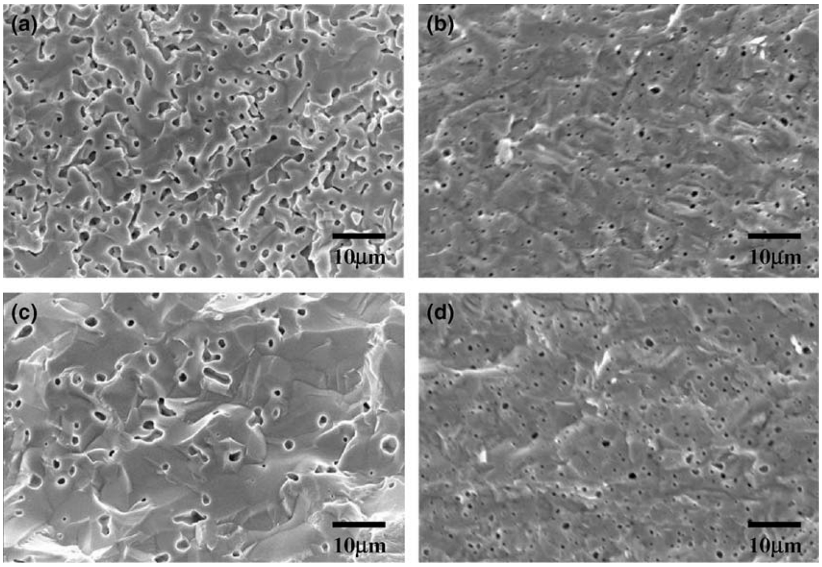

Fig. 5. Fractured surface of sintered Dy_2TiO_5; (a) SS process, (b) EG process at 1500 °C and (c), (d) at 1600 °C, respectively.

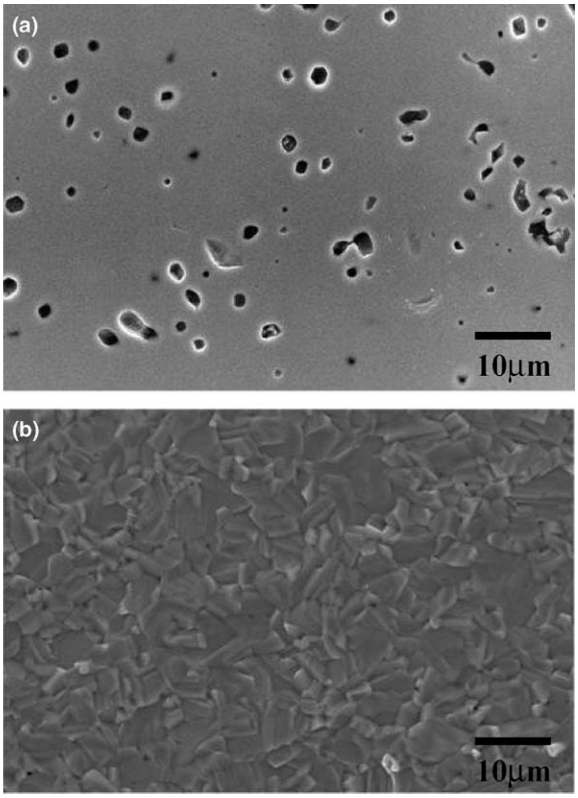

Fig. 6. Polished surface of sintered Dy_2TiO_5; (a) SS process and (b) EG process at 1600 °C, respectively,

a broad grain size distribution of 3–5 μm grains with a few small pores located on grain boundaries. However, the polished surface of SS samples showed large grains (>20 μm) surrounded by 2–3 μm pores.

The sinterability, such as density, microstructure of grains and pore size, is an important aspect of the powder properties. For the same composition of the powder, the sinterability depends on the temperature of sintering, green density, external pressure, particle size and sintering additives. The stage of sintering at 1500 °C for the pellet from EG powder was caused by the highly sinterable and submicron-sized particles [12]. The pellet made by SS did not show such a stage of sintering which confirmed this point.

At a given temperature, the green compacts prepared from the EG powders were densified to higher densities and a uniform microstructure even without the CIP process in a comparison with the green compacts prepared from the SS powders. This is because the EG powders have smaller particle size and higher surface area by the special powder synthesis process involving polymer compared to those of the SS powders.

4. Conclusions

A new polymer route for the synthesis of Dy_2TiO_5 ceramic powders was successfully developed. Submicron-sized crystalline particles were directly synthesized by the EG process without going through the intermediate processes in a short time. The compounds crystallized in the orthorhombic structure up to 1300 °C. With a calcination temperature increase, it transforms into the hexagonal phase (~1500 °C). The synthesized Dy_2TiO_5 powders had a high purity and a good sinterability, which could be reached with 95% TD at 1500 °C for 2 h. The products obtained through the EG process were found to be stable crystalline and highly sinterable powders that are suitable for control rod material.

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