Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 373 (2008) 194–198

journal of nuclear materials

www.elsevier.com/locate/jnucmat

A polymer solution technique for the synthesis of nano-sized Li_2TiO_3 ceramic breeder powders

Choong-Hwan Jung [a,*], Sang Jin Lee [b], Waltraud M. Kriven [c], Ji-Yeon Park [a], Woo-Seog Ryu [a]

[a] Nuclear Materials Technology Development Division, Korea Atomic Energy Research Institute, Daejeon 305-600, Republic of Korea
[b] Department of Advanced Materials Science and Engineering, Mokpo National University, Muan 534-729, Republic of Korea
[c] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61821, USA

Received 15 August 2006; accepted 23 May 2007

Abstract

Nano-sized Li_2TiO_3 powder was fabricated by an organic–inorganic solution route. A steric entrapment route employing ethylene glycol was used for the preparation of the nano-sized Li_2TiO_3 particles. Titanium isopropoxide and lithium nitrate were dissolved in liquid-type ethylene glycol without any precipitation. With the optimum amount of the polymer, the metal cations (Li and Ti) were dispersed in the solution and a homogeneous polymeric network was formed. The organic–inorganic precursor gels were turned to crystalline powders through an oxidation reaction during a calcination process. The dried precursor gel showed the carbon-free Li_2TiO_3 crystalline form which was observed above 400 °C. The primary particle size of the carbon-free Li_2TiO_3 was about 70 nm, and the structure of the crystallized powder was porous and agglomerated. The powder compact was densified to 92% of TD at a relatively low sintering temperature of 1100 °C for 2 h.

1. Introduction

Lithium-containing ceramics have been considered as tritium breeding materials of the ITER test blanket module (TBM) for the DEMO reactor [1]. To date, considerable work has been done on the fabrication of Li_2TiO_3 pebbles, characterizing the tritium release behavior and developing a properties database [2–4]. The previous research has shown that Li_2TiO_3 has attractive properties that are better than those for other lithium-containing compounds. Li_2TiO_3-sintered body can be prepared by various methods. The most commonly employed method is an indirect mixing of the two oxides followed by compaction and sintering [5]. For this application, highly sinterable Li_2TiO_3 through a processable powder-synthesis method is necessary.

Ceramic powder processing is evolving in the direction of a chemical synthesis of the powders [6]. Methods based on a soft-solution processing provide powders with the desired properties. Recently, an organic–inorganic solution technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG ($HOCH_2CH_2OH$, ethylene glycol) as a polymer carrier has been developed to make the soft-solution processing easier and more productive [7–15]. The polymer ensures a homogeneous distribution of the metal ions in its polymeric network structure and it inhibits their segregation or precipitation from the solution. In the solution involving a polymer and nitrate ions, a continuous long chain polymer prevents a contact between the cations and it limits their agglomeration and precipitation [9–19]. In a water–soluble system, the PVA polymer only works with systems. However, by applying an EG polymerizing agent, the process can be extended to chemicals that decompose in water, such as metal-alkoxide (titanium isopropoxide). In particular, the ethylene glycol can act as an

---

[*] Corresponding author. Tel.: +82 42 868 8567; fax: +82 42 862 5496. *E-mail address:* chjung1@kaeri.re.kr (C.-H. Jung).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.05.050

effective solvent for a wet chemical synthesis of a titanate powder because the water–soluble titanium salt is not available commercially [16,20]. At the optimal amount of an EG polymer, the metal ions are dispersed in a solution and a homogeneous polymeric network is formed.

In the present study, nano-sized Li_2TiO_3 powder is prepared by the EG method, and the effect of the polymer content, the crystallization behavior and the powder morphology are examined.

2. Experimental procedure

Titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$, TISO, Alfa Chem.) and lithium nitrate ($LiNO_3$, Aldrich Chem.) were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chem.). The amount of EG was calculated by using a ratio of the total weight of the metal ions from cation sources to weight of the EG. In this experiment a 1:4 ratio was tried. 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. The inside of the furnace was monitored through a window in the low temperature range (100–300 °C) to observe the explosive reaction. Finally, the calcined powders were planetary milled with a dia 5 mm zirconia media for 12 h. Isopropyl alcohol was used as a solvent for the milling, and the milling speed was 200 rpm.

The crystallization behavior of the gel-type precursor powders was examined as a function of the temperature, by using an X-ray diffractometer, with a scanning speed of 4°/min and a sampling interval of 0.02°. The crystallite size of the particles was calculated using the following Scherrer's equation from XRD data, $B - b = (\kappa \cdot \lambda)/(d \cdot \cos\theta)$, where, B is the half-value breadth (rad), b is the half-value breadth for materials of which crystallite size is larger than 100 nm, κ is the shape factor ($\kappa = 0.9$ at sphere), λ is the wave length of X-ray (Cu Kα; $\lambda = 0.15418$ nm), d is the crystallite size of Li_2TiO_3 (nm) and θ is the angle of diffraction (rad). The pyrolysis and decomposition behavior of the dried precursor were monitored by DTA-TG up to 1000 °C at a heating rate of 10 °C/min in an air atmosphere. The morphologies of the porous, crystallized powder and planetary milled powders were examined by scanning electron microscopy. Fig. 1 shows the details of the preparation process. In the case of pebble preparation, the polyvinylalcohol (PVA) solution was fabricated by dissolving 2 wt% of PVA in deionized water and spraying it onto the calcined and milled powders while they were being rolled with 150 rpm in a plastic jar. The primary wet-powder was sieved with 50 mesh screen. The sieved powder took the shape of granule-type spheres. For high-green density pebbles, these spheres were rolled again for several hours at various rolling speeds.

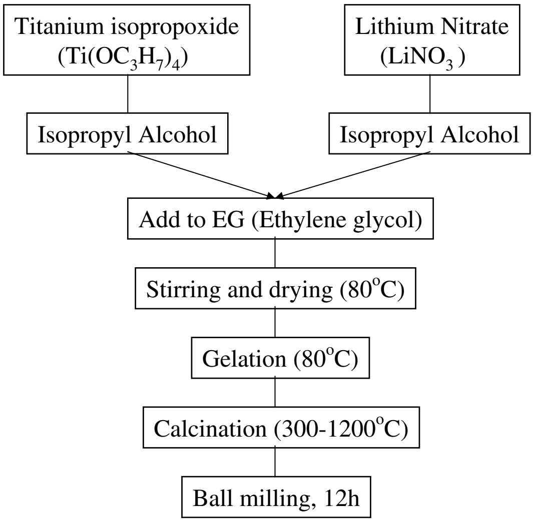

Fig. 1. Schematic diagram of the ethylene glycol method.

3. Results and discussion

During the synthesis of lithium monotitanate, soft-precipitates were formed in the solution of the ethylene glycol containing Ti-isopropoxide, due to the water in the precursor solution but they were dissolved after a stirring. The precursor solution with dissolved titanium isopropoxide and lithium nitrate has a pale yellow color. During the drying process at 80 °C, the transparent sol turned to a soft gel. The application of heating to the gel resulted in a charred foam structure.

Simultaneous DTA/TG results of the precursor gel from room temperature to 1000 °C are given in Fig. 2. In the TGA curve, the mass change occurred in three stages (1) 135 °C to 191 °C, (2) 210 °C to 257 °C and (3) 260 °C to 300 °C. The DTA showed two exothermic peaks at 170 °C and 235 °C, and one endothermic peak at 280 °C. In general, polymer decomposition occurs by two steps [21]. The first step is degradation of the polymeric structure by pyrolysis, which is then followed by oxidation of residual carbon. In the EG method, the first mass change was due to pyrolysis of EG resulting in breaking of bonds, removal of free organics from metal-ion sources and release of N_xO_y gases. An exothermic at 235 °C in the

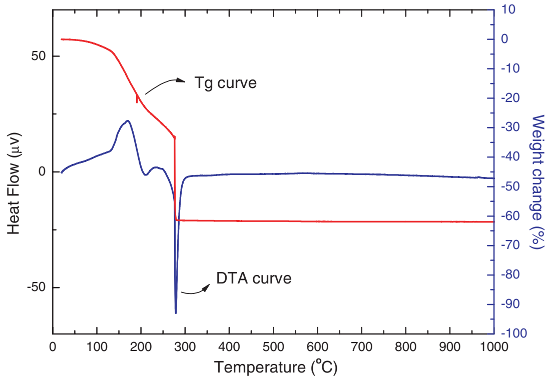

Fig. 2. DTA/TG curves for the dried precursor prepared by the ethylene glycol method (mass ratio of metal ions to EG is 1:4).