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Preparation and characterization of lithium–titanate pebbles by solid-state reaction extrusion and spherodization techniques for fusion reactor

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ABSTRACT

For the development of TBM for fusion reactors, lithium containing ceramics as against the metal are preferred as tritium breeding material. Lithium titanate (Li_2TiO_3) is one such chosen ceramic tritium breeder. Li_2TiO_3 pebbles are conventionally prepared by sol–gel process and wet process. Solid state reaction of lithium carbonate with titanium dioxide is preferred route for the bulk production of Li_2TiO_3. Thermo-gravimetric and differential thermal analysis (TG–DTA) techniques have been used in the present study to understand the solid state reaction of intimate mixture of lithium carbonate and titanium dioxide. It was found out that single phase lithium titanate (Li_2TiO_3) is produced at 750 °C and the reaction is completed in 6 h. Fine powders of lithium titanate obtained after milling and classification were mixed with aqueous solution of PVA to prepare green pebbles of desired size and shape. The pebbles were subsequently sintered at 900 °C and the effect of sintering time on the properties of sintered pebbles was studied. The reaction mechanisms and the product qualities obtained by the solid state reaction, extrusion and spherodization techniques are discussed in this paper.

1. Introduction

Lithium-containing ceramics such as lithium oxide (Li_2O), lithium aluminates ($LiAlO_2$), lithium–titanate (Li_2TiO_3), lithium silicate (Li_4SiO_4) and lithium zirconate (Li_2ZrO_3) have been considered as tritium breeding materials for the ITER test blanket module (TBM) and also for DEMO reactor [1–3]. Li_2TiO_3 is one of the suitable material for TBM [4,5] due its attractive properties, such as the high lithium density, high thermal stability, tritium release at low temperature, and high thermal conductivity [6] as compared with lithium–zirconates (Li_2ZrO_3), and lithium–silicate (Li_2SiO_4). Till date, much work has been done on the fabrication of Li_2TiO_3 pebbles, characterization of pebbles, tritium release behavior [7,8] and developing a database for properties [9]. Various investigators have proposed different methods for the fabrication of Li_2TiO_3 pebbles. The most commonly adopted methods are: mixing of the two oxides followed by compaction and sintering [10], wet process and sol–gel process [11–15].

The sol–gel and the wet process are the most preferred methods for Li_2TiO_3 pebble fabrication, but reprocessing of effluent is necessary for effective utilisation of resources and reduction of waste [14]. In the wet process, chilled acetone media is used for the pebble fabrication from a liquid mixture of Li_2TiO_3 and PVA solution. The pebbles are heated at 650 °C for 6 h and sintered at 1400 °C for 4 h [14]. A solid phase reaction of Li_2CO_3 and TiO_2 was carried out at 1400 °C followed by extrusion, spherodization and sintering. The Li_2TiO_3 microspheres have 62% of theoretical density (TD), which is 3.43 g/cm^3 of a single crystal [16]. Lithium density is a dictating parameter in the economy of fusion reactor [17]. A stoichiometric mixture of $CH_3COOLi·2H_2O$ and TiO_2 was calcined at 500 °C to obtain an intermediate, comprising Li_2TiO_3 and unreacted titanium-dioxide. After milling the product, amino acid, glycine, alanine (ALA), or L-phenylalanine (PHE) were added and the mixture was further milled and again calcined at 700 °C for 1 h to obtain $Li_4Ti_5O_{12}$ with a phase purity above 97% for the achievable average particle size of $Li_4Ti_5O_{12}$ 70 nm ± 10 nm. The mechanism and significance of the two-step calcination coupled with mechanical activation and addition of an amino acid to the intermediates were discussed [18–22]. In an earlier attempt the synthesis of Li_2TiO_3 was carried out by solid state reaction of a homogeneous mixture

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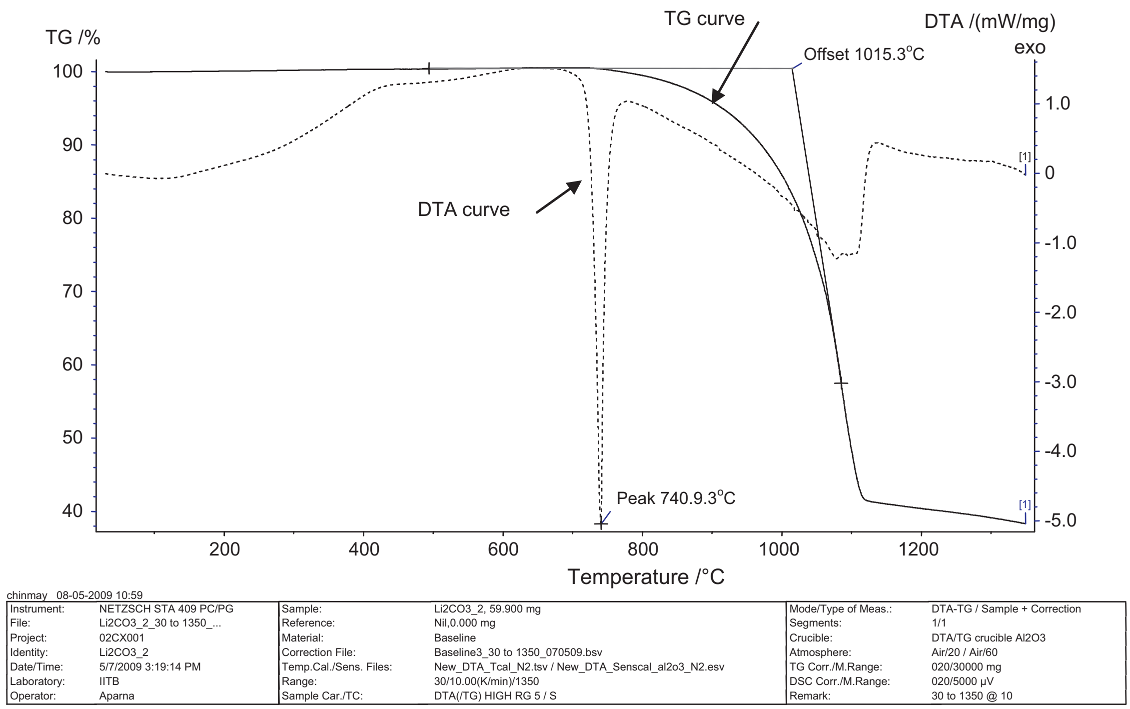

Fig. 1. TG–DTA of Li_2CO_3 (30–1300 °C), rate of temperature increase 10 °C per minute.

of Li_2CO_3 and TiO_2 at 900 °C for 8 h and calcination was carried out in two stages to ensure complete reaction [23,24].

The process consists of the process sequence, 'mixing and milling, classification, sample preparation and calcination, milling, pebble fabrication, and sintering'. Li_2TiO_3 was first synthesized by the solid state reaction of Li_2CO_3 and TiO_2 (1:1 mole ratio) at 750 °C for 6 h. Compared to the previous study [23,24] the reaction was carried out at 750 °C instead of 900 °C and reaction time allowed 6 h instead of 8 h. Moreover, reaction was carried out in single stage in the present study compared to the two stages in previous study [23,24]. The reacted mass was milled and sieved. The fine particles of size <45 μm were mixed with aqueous solution of poly-vinyl alcohol (PVA) to fabricate spherical shaped pebbles by the extrusion, followed by spherodization. The green pebbles were dried at 500 °C for 2 h to remove PVA and then sintered at 900 °C for 6 h.

The detailed process and characterization of the pebbles are presented and discussed in this paper. The feasibility of producing high density Li_2TiO_3 pebbles having ideal microstructure over a short time even at a relatively low temperature is presented here.

2. Experimental procedures

2.1. TG and DTA

TG–DTA techniques were used to study the decomposition of pure Li_2CO_3 and reactivity of intimately mixed powders of Li_2CO_3 and TiO_2. The TG–DTA experiments were carried out in Netzsch TG–DTA (Model STA 409 PC/PG) and rate of temperature increase was 10 °C per minute. It was observed that pure Li_2CO_3 does not have any significant weight loss until 700 °C. The TG and DTA curves of pure Li_2CO_3 (Fig. 1) indicate that decomposition of Li_2CO_3 starts at 740.9 °C. The DTA curve shows one endothermic peak corresponding to the temperature of 740.9 °C.

Fig. 2 shows the TG and DTA curves of Li_2CO_3–TiO_2 system (1:1 mole ratio). The TG-curve shows that the reaction of Li_2TiO_3–TiO_2 mixtures starts at 600 °C, i.e. it precedes the decomposition of pure Li_2CO_3 by about 140 °C. Hence, it seems that Li_2CO_3 reacts with TiO_2 even before the decomposition and the following reaction (1) takes place.

$$Li_2CO_3(s) + TiO_2(s) = Li_2TiO_3(s) + CO_2(g) \quad (1)$$

2.2. Li_2TiO_3 synthesis and pebble fabrication

Form the TG–DTA analysis it is concluded that reaction is complete at 750 °C. This result indicates there is no need for higher temperature >750 °C for Li_2TiO_3 pebble fabrication from the solid state reaction of Li_2CO_3 and TiO_2.

The process steps followed are, 'mixing and milling, classification, sample preparation and calcination, milling, pebble fabrication, and sintering'. These process steps are described below.

2.2.1. Mixing and milling of Li_2CO_3 and TiO_2

Anatase TiO_2 (analytical grade, SD Fine Chem., Product code: 90446) and Li_2CO_3 of 99.0 purity (Merck, CAS No: 554-13-2) were taken in stoichiometric ratio and milled in a planetary ball mill for 5 h.

2.2.2. Classification

The intensely mixed and milled powders were classified in a vibratory sieve shaker. Particles size less than 45 μm were separated and oversized were re-cycled in the ball mill.

2.2.3. Sample preparation and calcination

The mixed powders were put in alumina crucibles and small quantity of absolute methanol was added to make a paste and kept overnight. The crucibles containing homogeneous mixture of titanium-di-oxide and lithium–carbonate were kept in a muffle furnace. The temperature was increased up to 750 °C in 2 h and maintained for 6 h.

2.2.4. Milling

The product was cooled, grounded to fine particle sizes of approximately 45 μm in planetary ball mill.