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Sintering characterization of Li_2TiO_3 ceramic breeder powders prepared by the solution combustion synthesis process

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Abstract

A new approach, the solution combustion synthesis process (SCSP), has been developed to produce high purity and fine-grained Li_2TiO_3. The synthesis using glycine as a fuel was studied in order to prepare the powders that could be sintered to the 80% TD at relatively low temperature (<1100 °C) and short sintering time (<4 h). Systematic studies were carried out to optimize various parameters such as sintering temperature, time and the microstructure of the sintered pellets. The SCSP was shown to be a practically viable process to prepare highly pure and sinterable Li_2TiO_3 powders.

1. Introduction

A number of lithium related ceramics such as $LiAlO_2$, Li_2ZrO_3 and Li_2TiO_3 have been considered as candidates for tritium breeding materials in D–T fusion reactors [1–3]. Li_2TiO_3 is a low-activation material for use in this field. To date, much work has been done on the fabrication of Li_2TiO_3 pebbles, characterizing the tritium release behavior and developing the properties database [4,15,16]. Finn et al. [5] performed early research which showed that Li_2TiO_3 has attractive properties, such as the same lithium density as that for Li_2ZiO_3, and its melting point is similar. The thermal conductivity is better than that of the aluminates or the zirconates. Long-term waste problems should be low because titanium is a low-activation element, and it appears as the best material with a temperature for the tritium release maximum inferior to 300 °C [4]. Li_2TiO_3 pellets can be prepared by various methods. The commonly employed methods are (i) direct mixing of the two oxides followed by compaction and sintering and (ii) sol–gel techniques [11].

Recently, a novel powder preparation method based on the solution combustion synthesis process (SCSP) using glycine or mixed organics as the fuel was successfully developed in our group for the preparation of high purity, very active and nano-crystalline $LiAlO_2$, Li_2ZrO_3, and Li_2TiO_3 powders [12,14]. In the present study, the feasibility of preparing Li_2TiO_3 that can be compacted and sintered to high densities at a relatively low sintering temperature and short sintering time in order to have an ideal microstructure and to reduce the overall production costs using solution combustion synthesis.

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2. Experimental procedure

All reactants for the solution combustion synthesis must be soluble in water. Anions for the salts as reactants should decompose easily upon heating. The anions good for the processing are metal-nitrate, however, chloride and sulphate should be avoided, as they will remain in the product as impurity after the combustion processing. The powder preparation method of Li_2TiO_3 has been described previously [12]. Aqueous solutions of $LiNO_3$ and $TiO(NO_3)_2$ were prepared as a stock solution. The precursor solution for combustion was prepared by adding a stoichiometric amount of glycine as a fuel to the above stock solution. The combustion process was performed by heating the stock solution in air on a hot plate. After the water has fully vaporized, spontaneous ignition started by burning of metal-nitrate and fuel.

The sinterability of the combustion-derived powders (hereafter called CPs) was studied by measuring the sintered density and dimensional shrinkage with temperature. The samples were prepared by pressing at 300 MPa into 10 mm diameter and 3 mm thick pellets. No binder or lubricant was added for the preparation of the compacts. As a reference, Li_2TiO_3 pellets were prepared by two other methods; cold pressing of commercially available powders (Aldrich Co., hereafter called APs) and the solid-state reacted powders (hereafter called SPs) were also made by mechanical mixing and calcinations of the Li_2CO_3 and TiO_2 mixtures. The mixed powders were blended up by a three-axis mixer for 2 h using zirconia-grinding media with ethanol, after drying at 100 °C for 24 h, placed in an alumina crucible and calcined at 700 °C for 3 h. The relative density of sintered samples was measured by Archimedes' method. The crystalline structure of as-synthesized powders were determined using X-ray diffractometry with Cu Kα radiation (Rigaku), and scanning electron microscopy (SEM, JEOL), operating at 35 kV accelerating voltage. The linear thermal expansion of the compacted pellets (10 mm dia. and 3 mm thickness) was measured using a dilatometer in the temperature range of 20–1350 °C with a heating rate 4 °C/min in air. Simultaneous thermogravimetry and differential thermal analysis (TG/DTA) and DSC (differential scanning calorimeter) analysis were performed using a Setaram TG/DTA model.

3. Results and discussion

3.1. Formation of Li_2TiO_3 powder by various processes

The powder synthesis process by solid-state reaction (SPs) is the most well known method for the synthesis of oxide ceramics. A stoichiometric mixture of titania (TiO_2, anatase) and lithium carbonate (Li_2CO_3) was used. Fig. 1 shows the DSC analysis for this mixed powder under air condition, the broad endothermic range of 300–700 °C is presented which is associated with the reaction of Li_2CO_3 and TiO_2 as follows, $Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2\uparrow$. This reaction was completed at 700 °C at least after 3 h. The XRD patterns of SPs with various calcination temperatures have been presented previously [12].

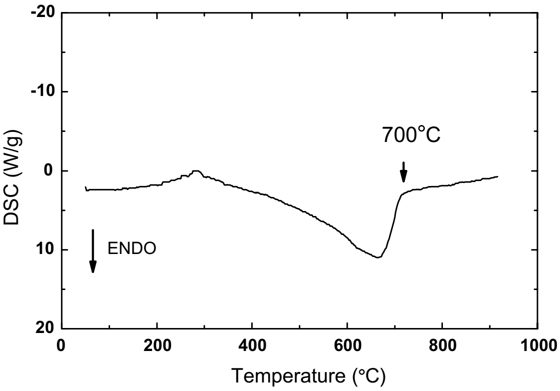

Fig. 1. DSC curve of solid-state reacted $LiCO_3$ and TiO_2 mixture.

The general combustion process can be explained as follows. The precursor solution contains the oxidizers (metal salts) and the readily combustible fuel such as glycine or urea. On heating the precursor solution after water evaporation, the nitrate decomposed giving oxides of nitrogen (NO_x). The homogeneous and exothermal oxidation-reduction reactions of gas-phases increase the temperature of the intact viscous mixture immediately adjoining to the combustion zone causing reaction. The reaction process proceeds rapidly and sustains until the entire intact zone is consumed. The rapid temperature increase with the orange flame and the volume of gas generated during the reaction depend on the fuel type, composition and content; in general, a stoichiometric composition gives rise to higher temperature and to evolute more gases [6–10,12]. Fig. 2(a) and (b) show the TG/DTA curve for the mixtures of the stoichiometric ratio of $LiNO_3$ and $TiO(NO_3)_2$ without and with fuel (in case of glycine). In Fig. 2(a), the three broad endothermic peaks at 165, 270 and 600 °C were indicated as the removal of bonded water and the decomposed the Li- and Ti-nitrate, respectively. In Fig. 2(b), however, this exhibited a highly exothermic event with a major weight loss (about 85%) starting at 292 °C and there were no further thermal events up to 400 °C, therefore, this is the ideal result for the solution combustion synthesis. The endotherms from 80 to 250 °C may be explained as the removal of loosely bound absorbed or chemically bonded water. The overall weight change in the sample after exothermic event at

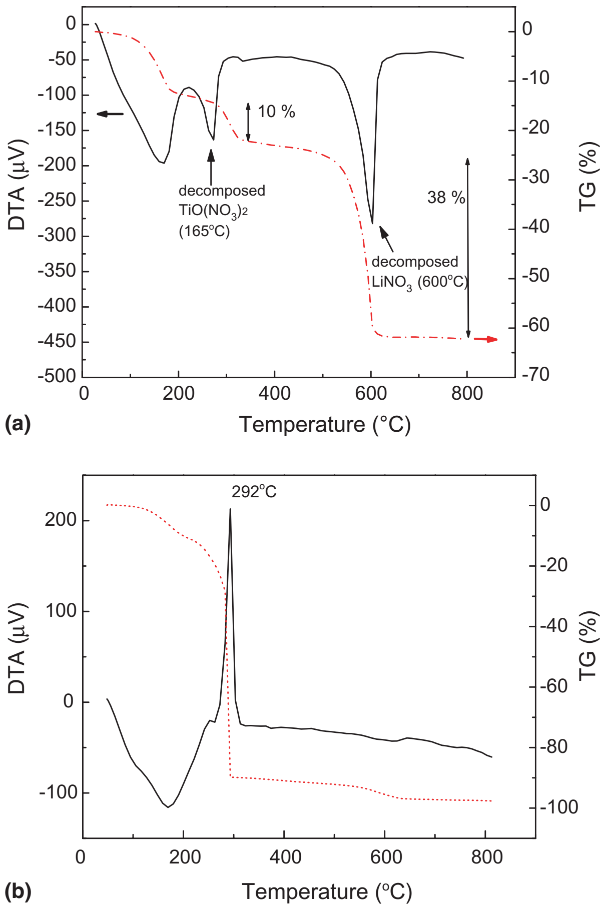

Fig. 2. TG/DTA curve of (a) $LiNO_3 + TiO(NO_3)_2$ without fuel and (b) glycine-fueled precursor in air.

292 °C was less than 5% and weight of the sample remained constant until 800 °C as shown by TGA. The most important aspect evident from the thermal studies is the absence of enthalpy changes at high temperatures, which implies that the combustion reaction is complete and no organic matters or un-reacted phases are present in the sample, and there is no evidence of a phase transition taking place in the sample up to a temperature of 800 °C.

Fig. 3 shows the SEM micrographs of the CPs and SPs, respectively. The microstructure of SPs consists of grains of aggregates, that of CPs reflects the foam and has a lot of pores which may be formed by the evolved gases during combustion.

3.2. Sintering behavior of Li_2TiO_3

In order to investigate the sintering behavior of the pellets prepared by the solution combustion synthesis and other different methods, the thermo-dilatometry analysis (TDA) and the derivative of thermo-dilatometry analysis were performed up to 1300 °C at a constant heating rate (4 °C/min) in static air atmosphere. Green pellets were made by pressing of powder in a die, 10 mm in diameter and 3 mm thickness. The calculated green density after cold isostatic pressing was 1.88 g/cm^3, corresponding to 55% of theoretical density.

The shrinkage behavior in air atmospheres was plotted in the form of percentage of shrinkage $[(dL/L_0) \times 100]$ versus temperature, where L_0 is the initial length. The result is shown in Fig. 4. As shown by thermo-dilatometric curves (Fig. 4), a rapid decrease of length was observed above 600 °C for combustion synthesized samples, however, the length shrinkage of commercial and solid state samples started at about 850 °C. Consequently, sintering of the combustion synthesized samples takes place between 600 and 1200 °C with 20% of linear shrinkage (A in Fig. 4). However, the densification is not entirely achieved at 1300 °C for commercial (B in Fig. 4) and solid-state reacted samples (C in Fig. 4). The sinterability is an important aspect of the powder properties. For powder of the same composition, the sinterability depends on the temperature of sintering, green density, external pressure, particle size and

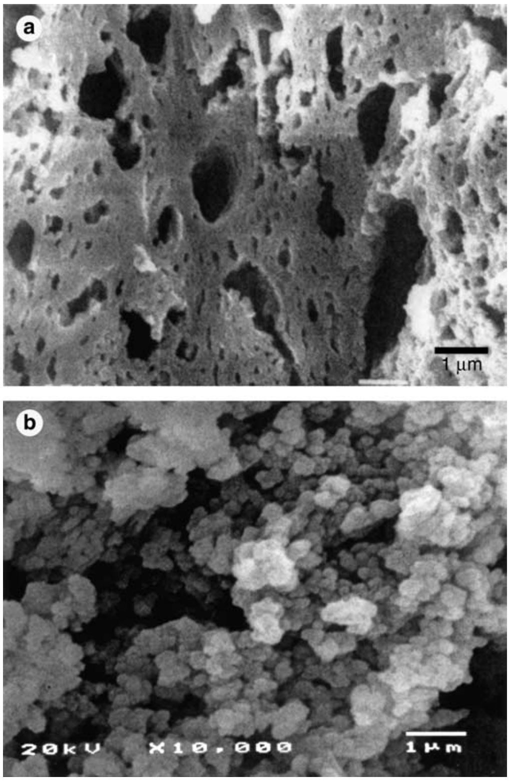

Fig. 3. SEM micrographs of the Li_2TiO_3 powders made by (a) combustion synthesis and (b) solid-state reaction.

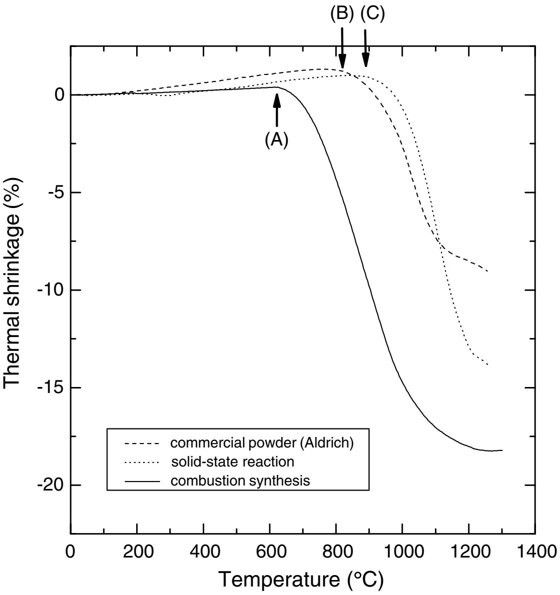

Fig. 4. Shrinkage curves of Li_2TiO_3 pellets in air atmospheres. The thermal shrinkage (%) values are plotted against temperature.

sintering additive. The stage of sintering below 850 °C for the combustion-synthesized powders was caused by the ultra-fine particles [12,13]. The pellets made by SPs and APs (Aldrich) did not show such a stage of sintering which confirmed that point.

In order to examine the effect of sintering temperature and time on the densification of as-prepared pellets, the green compacts fabricated from CPs, APs and SPs were sintered at temperatures varying from 800 to 1300 °C, respectively. The relative density of the pellets is shown in Fig. 5. In general, the increase of sintering temperature increases the density of the compacts, irrespective of the composition of the solid solutions. It is seen from Fig. 5 that the compacts of CPs could be sintered to >80% TD at 1000 °C. The optimum temperature and time for sintering Li_2TiO_3 powders derived through a combustion process using glycine are 1100 °C and 4 h, respectively. At given temperature, the green compacts prepared from combustion-derived powders sinter to higher densities compared to the green compacts prepared from the solid-state reaction or commercial powders and reference results. This is because the combustion-derived powders have a small particle size and higher surface areas and relatively larger soft particles with high porosity compared to those of solid-state reaction or commercial powders. The combustion-derived powder has a smaller crystallite size which helps the acceleration of sintering at lower temperature with the result that no further sintering occurs at high temperatures. The combustion-derived products could be sintered to high density at lower temperature and shorter sintering time, indicating the reactive nature of the combustion-derived powders. Li_2TiO_3 pellets using the combustion synthesized powders sintered to 82% TD at 1000 °C for 4 h. An etched SEM micrograph

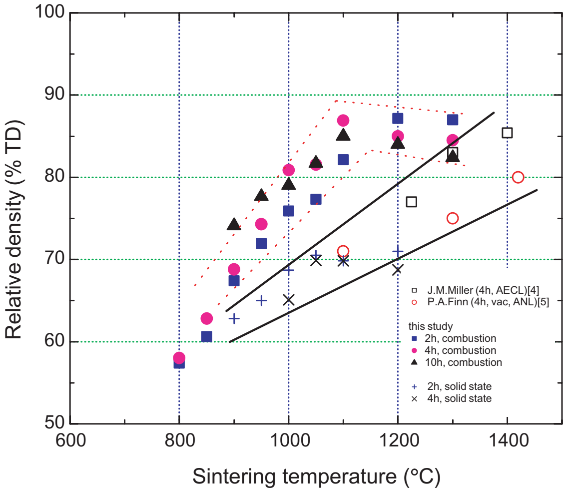

Fig. 5. Relative density of Li_2TiO_3 pellets synthesized by the various process.

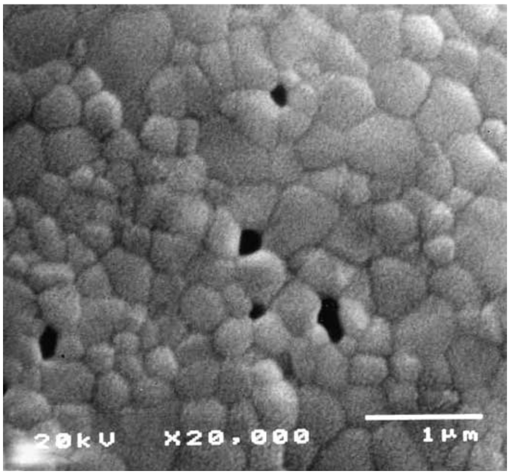

Fig. 6. SEM micrograph of the Li_2TiO_3 pellet synthesized by combustion reaction and sintered at 1000 °C for 4 h.

of a sintered Li_2TiO_3 pellet is shown in Fig. 6. The microstructure of Li_2TiO_3 reveals the presence of pores, and the average grain size is 0.5 μm.

4. Conclusion

Ultra-fine crystalline Li_2TiO_3 particles were synthesized by direct solution combustion synthesis without going through intermediate processes using Li and Ti-nitrate of stoichiometric composition of the fuels in a short time. The synthesized lithium titanate powders had a high purity and a good sinterability, which could be reached to 85% TD at temperatures as low as 1100 °C for 4 h. The products obtained through the combustion synthesis were found nanocrystalline and of high sinterability, and the porous powders were found to be suitable as fusion breeder material for making high density pebbles.

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