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A promising tritium breeding material: Nanostructured $2Li_2TiO_3$-Li_4SiO_4 biphasic ceramic pebbles

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As an advanced tritium breeder material for the fusion reactor blanket of the International Thermonuclear Experimental Reactor (ITER), Li_2TiO_3-Li_4SiO_4 biphasic ceramic has attracted widely attention due to its merits. In this paper, the uniform precursor powders were prepared by hydrothermal method, and nanostructured $2Li_2TiO_3$-Li_4SiO_4 biphasic ceramic pebbles were fabricated by an indirect wet method at the first time. In addition, the composition dependence (x/y) of their microstructure characteristics and mechanical properties were investigated. The results indicated that the crush load of biphasic ceramic pebbles was better than that of single phase ceramic pebbles under identical conditions. The $2Li_2TiO_3$-Li_4SiO_4 ceramic pebbles have good morphology, small grain size (90 nm), satisfactory crush load (37.8 N) and relative density (81.8 %T.D.), which could be a promising breeding material in the future fusion reactor.

1. Introduction

Lithium based ceramics have been considered as the most prominent tritium breeder material in test blanket modules (TBM) of ITER. Both Li_4SiO_4 and Li_2TiO_3 are extensively used due to low activation, chemical stability and favorable tritium release properties. Nevertheless, Li_2TiO_3 owns better mechanical properties but lower lithium content than that of Li_4SiO_4, whereas the latter is sensitive to moisture and easily absorbs CO_2 [1–3]. To realize advantageous complementarities, Li_2TiO_3-Li_4SiO_4 biphasic ceramic pebbles have gradually attracted our attention. For example, R. Knitter [2] fabricated Li_2TiO_3-Li_4SiO_4 pebbles via melt-spraying method by adding TiO_2, the result indicated that the fabricated two-phase pebbles exhibited a fine-grained microstructure and the crush load of the pebbles was significantly enhanced compared to Li_4SiO_4. Besides, the grain size of ceramic decreased with the increasing of Li_2TiO_3 content. Maoqiao xiang [4] prepared Li_2TiO_3-Li_4SiO_4 pebbles by a graphite bed process, the average crush load of 50%Li_2TiO_3-50%Li_4SiO_4 pebbles sintered at 1100 °C was up to 104.79 N, whereas the grain size had increased to 1.67 μm. It is strongly illustrated that composites with a second phase dispersed in matrix have higher strength compared to the single phase.

Moreover, the grain size plays an important role in the tritium release properties of tritium breeding ceramics. The tritium release properties may be enhanced by decreasing grain size [5–8]. Casadio et al. [9] announced that tritium release rate increased by decreasing grain size of Li_2TiO_3 pebbles (above 85 %T.D.), which had been confirmed by the out-of-pile tritium annealing studies on Li_2TiO_3 pebbles. H. Wedemeyer et al. [10] conducted the annealing studies and in-pile test, which clearly demonstrated tritium relase is faster for small grained (about 7 μm) than for the large grained (about 80 μm). The residence time for the large grained Li_4SiO_4 at 600 °C is about ten times longer than for the small grained material. Furthermore, the mechanical properties can be enhanced by decreasing grain size [11]. Additionally, nanomaterials show an excellent radiation resistance which can alleviate the swelling, embrittlement and fragment of tritium breeding ceramics under radiation environment [12]. Meanwhile, one of the challenges in processing these materials is to meet the requirements of nanostructure and density at the same time during sintering process. A low sintering temperature is a necessary, but not a sufficient

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condition for achieving the required microstructure [13]. Multi-phase ceramic can refrain excessive grain growth due to the pinning effect of every phase [14]. Therefore, preparing Li_2TiO_3-Li_4SiO_4 biphasic ceramic is an efficient way to acquire preferable mechanical properties, which is an important factor in the design of tritium breeding material. Various and significant advantages make biphasic nanoceramic possible to be the optimal choice in new generation tritium breeder materials. Even though there were some papers concerning about the fabrication of Li_2TiO_3-Li_4SiO_4 ceramic pebbles, there was no literature about the fabrication of nanostructured biphasic lithium ceramic pebbles until now.

In this paper, Li_2TiO_3-Li_4SiO_4 biphasic nanoceramics were fabricated by an indirect wet method. Besides, the proposed fabrication method is eco-friendly as it avoids using organic additives. The microstructure and mechanical properties of different component ceramic pebbles were also investigated.

2. Experiment procedure

2.1. Preparation of precursor powder

Lithium hydroxide ($LiOH \cdot H_2O$ AR, 99%), fumed silica (SiO_2 AR, 99%) and titanium dioxide (Anatase TiO_2 AR, 99%, 5-10 nm) were selected as raw materials. $LiOH \cdot H_2O$ (0.12 mol) was adequately dissolved in 80 ml mixed solvent. The mixed solvent was composed of deionized (DI) water and ethanol (the volume ratio of DI water/ethanol was1:1). After vigorous stirring for 10 min, TiO_2 and SiO_2 were added to form mixture solution. Then the mixture solution was transferred into a Teflon-lined stainless steel autoclave of 200 ml capacity, and hydrothermal reactions proceeded at 200 °C for 20 h. Eventually, the precursor powders could be obtained by drying the products at 70 °C without washing.

2.2. Fabrication of pebbles

The green body pebbles (GBP) were fabricated by wet method. Firstly, the precursor powder, ethyl alcohol and zirconium dioxide ball were mixed with a mass ratio of 1:2.63:20. The mixture was placed in a nylon jar and ball milled for 6 h. Secondly, the product after ball milling was dried without washing at 70 °C. Then, the precursor powder and deionized water with a mass ratio of 1:1 were uniformly mixed to form homogeneous slurry. Finally, the slurry was dropped into liquid nitrogen through a nozzle and green bodies were formed because of the effects of surface tension. Afterwards, the green body pebbles were transferred into a drying oven after drying in room temperature for a certain time. Ultimately, xLi_2TiO_3-yLi_4SiO_4 ceramic pebbles could be obtained by sintering GBP at 850 °C for 4 h in a muffle furnace.

3. Result and discussion

3.1. Characteristic of the precursor powder

The preparation of nanoceramics is based on the premise of precursor nanopowder. The morphology of precursor powder is displayed in Fig. 1a, which shows that the powder particles are uniformly dispersed with a particle size of 30–40 nm. Hydrothermal method shows a unique advantage in the synthesis of nanopowder [15–17]. In hydrothermal reactions, the dielectric constant and viscosity of the reaction solvent play an important role in the particle growth of the solute. In a solvent with low dielectric constant, the solute is easier to saturate. In addition, small crystallities are more stable in solvents with lower dielectric constant than in solvents with high dielectric constant [18,19]. Therefore, it is easier to form smaller particles by choosing suitable hydrothermal solvent. Moreover, it can be seen from Fig. 1b that the GBP possess homogeneous microstructure, which is conducive to gain smaller grain size during sintering process.

The thermogravimetry were performed to determine the minimum required temperature for preparing pure Li_4SiO_4 and Li_2TiO_3. As observed in Fig. 2a, the first mass loss below 100 °C should correspond to physically absorbed water or residue from the preparation of the powder, the second weight loss (up to ~ 350 °C) should be attributed to the crystal water, the mass loss occurred in the range of 350 °C–550 °C should represent the reaction between SiO_2 and Li_2CO_3 (Eq. (1)) and the decomposition of the residual LiOH. Li_2CO_3 was formed Li_2CO_3 by the reaction of LiOH and CO_2 during drying process. The mass loss in the range of 550 °C–600 °C should represent the formation of Li_4SiO_4 (Eq. (2)) [20]. The fifth mass loss (up to 800 °C) could be explained by the decomposition of the residual Li_2CO_3. The melting point of Li_2CO_3 is about 723 °C [21].

$$Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2\uparrow \tag{1}$$

$$Li_2CO_3 + Li_2SiO_3 \rightarrow Li_4SiO_4 + CO_2\uparrow \tag{2}$$

When the temperature exceeded 800 °C, weight loss hardly changed anymore. In recent designed TBM [22], the maximum service temperature of Li_4SiO_4 pebbles bed was 760 °C. In order to meet the requirement of increasing service temperature of TBM, the sintering temperature of ceramics ought to be as high as possible to prevent secondary growth of the grain during service process. To meet the requirements of phase purity and service temperature, 850 °C should be the optimal sintering temperature.

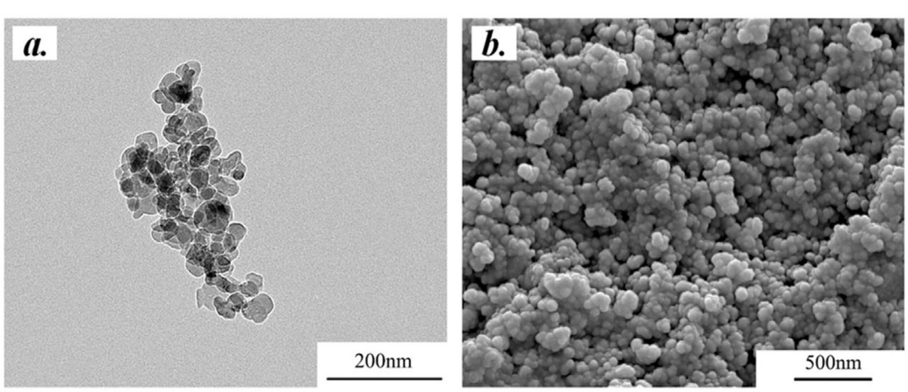

Fig. 1. (a)TEM image of the precursor powder (b)SEM image of the cross section of GBP.