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Effect of rapid sintering on the densification and the thermal diffusivity of Li_2TiO_3 pellet

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Abstract

Effect of a rapid sintering on the densification and the thermal diffusivity of undoped Li_2TiO_3 pellet has been studied and compared with those of TiO_2-doped Li_2TiO_3 pellet by using a push rod type vertical furnace and a laser flash method. The density of a rapidly sintered undoped Li_2TiO_3 pellet was remarkably increased and it was similar to those of the conventionally sintered TiO_2-doped Li_2TiO_3 pellets. The thermal diffusivity of the rapidly sintered undoped Li_2TiO_3 pellet was also increased. It was similar to those of the conventionally sintered TiO_2-doped Li_2TiO_3 pellets. Rapid sintering technique appears to be a possible means of improving the densification and the thermal properties of Li_2TiO_3 without a TiO_2 doping.

Keywords: Sintering; Li ceramic; Breeder

1. Introduction

Lithium-based ceramics, such as Li_2O, $LiAlO_2$, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3, are being considered as promising solid breeder materials in the tritium breeding blanket of thermonuclear fusion reactors. The breeder material plays an important role in producing tritium atoms by a lithium transmutation, $^6Li + n \rightarrow {}^4He + T$, where n is the neutron and T is the tritium. Among these candidates, Li_2TiO_3 has been recently recognized as the leading candidate because of its prominent tritium release rate at low temperatures between 200 and 400 °C [1,2] and its low activation characteristics.

Alvani et al. [3] reported that both the density and the grain size are key parameters in determining the tritium release rates. Provided the tritium release is not unduly affected, a higher density is favorable from the viewpoint of the lithium loading and the lithium-6 enrichment. The density of lithium-based ceramics also has an effect on its thermo-mechanical performance which is a critical issue for assessing the reliability of solid breeder blanket concepts over the lifetime of the component [4].

For dense pebbles with a low open porosity (above 85% of the theoretical density), the grain size plays a major role in the tritium release rate, which is increased by decreasing the grain size and consequently by increasing the grain boundaries. It is suggested that the microstructural requirements of the Li_2TiO_3 pebbles in the European Helium Cooled Pebble Bed (HCPB) Blanket design for a DEMO Fusion Reactor were 0.3–1.2 mm in diameter and ~90% of the theoretical density.

Many studies on manufacturing Li_2TiO_3 pebbles or pellets have reported that the sintering temperatures are from 1050 to 1400 °C and the sintering times are from 1 to 4 h. Lulewicz et al. [2] reported that a lithium deficient composition shows an improved microstructural stability and small grains during fabrication. However, there are few reports on the effect of the heating rate.

Rapid sintering, a sintering technique with a heating rate much faster than that in a conventional sintering, was proposed by Harmer and Brook [5] as a technique to suppress grain growth and to enhance densification. Recently, Chen and Wang [6] reported that fully dense cubic Y_2O_3 with a grain size of 60 nm can be prepared by simple two-step sintering, a modified rapid sintering technique. In this study, a rapidly heated two-step sintering technique was conducted in undoped and TiO_2-doped Li_2TiO_3 systems in order to increase the sintered density. The thermal diffusivities of the two kinds of samples prepared by the different sintering schedules were compared.

2. Experimental procedure

Samples of TiO_2-doped Li_2TiO_3 pellets were prepared from Li_2TiO_3 (Kosundo chemicals, 99.9% in purity) and TiO_2

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(Degussa, 99.9% in purity) powders. The 0, 5 and 10 mol% TiO_2-doped Li_2TiO_3 powder mixtures were wet-milled for 24 h in ethyl alcohol using a polyethylene bottle and high purity zirconia balls. The dried slurry was isostatically pressed under 200 MPa into cylindrical compacts of about 8 mm in diameter and about 10 mm in height. The green densities of the compacts were about 58% of the theoretical density. The shrinkage behavior of the 0%, 5% and 10% TiO_2-doped compacts in air was studied by using a push rod type dilatometer (Netzsch, Dil402C).

For the microstructural observation, the dried slurry was isostatically pressed under 200 MPa into discs of about 10 mm in diameter and about 2 mm in height. Some of the compacts were sintered at 1050 °C for 1 h in air. The heating rate used for the above studies was 5 K/min. Others were rapidly heated to 1300 °C, held for 10 min and immediately cooled to 1000 °C. And then they were annealed at 1000 °C for 1 h in air. The heating rate of the rapid sintering was about 150 K/min. The sintered density was measured using the water immersion method. The microstructure and crystalline form were determined by an optical microscope and X-ray diffraction (XRD), respectively.

Sintered pellets were ground to around 1 mm in thickness, 8 mm in diameter and polished slightly to prepare the thermal diffusivity measurement. The thermal diffusivity was measured in the temperature range of 298–773 K by using a Laser Flash Apparatus (Netzsch, LFA-427). The measurements of the thermal diffusivity were performed three times at every test temperature step in a vacuum (10^{-4} to 10^{-5} Pa).

3. Results and discussion

Fig. 1 shows the shrinkage behaviors of the 0%, 5% and 10% TiO_2-doped Li_2TiO_3 pellets in air plotted in the form of a percentage of the shrinkage versus the temperature. The onset of shrinkage occurs for the 0% TiO_2-doped Li_2TiO_3 at around 1000 °C. Those for the 5% and 10% TiO_2-doped Li_2TiO_3 occur at about 900 °C, which is about 100 °C lower than that for the 0% TiO_2-doped Li_2TiO_3.

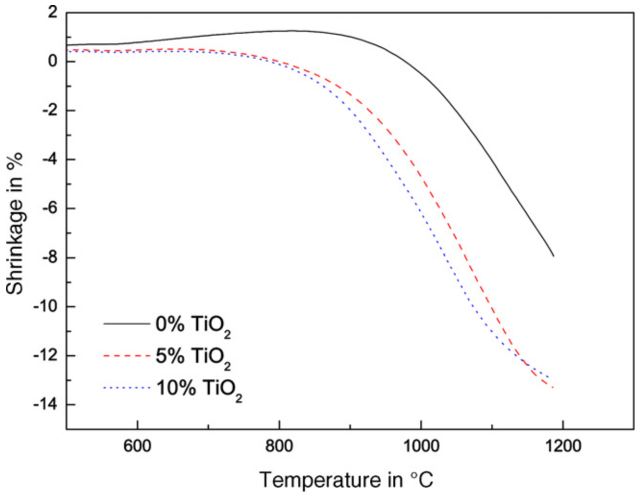

Fig. 1. Shrinkage curves as a function of the temperature for various TiO_2 contents.

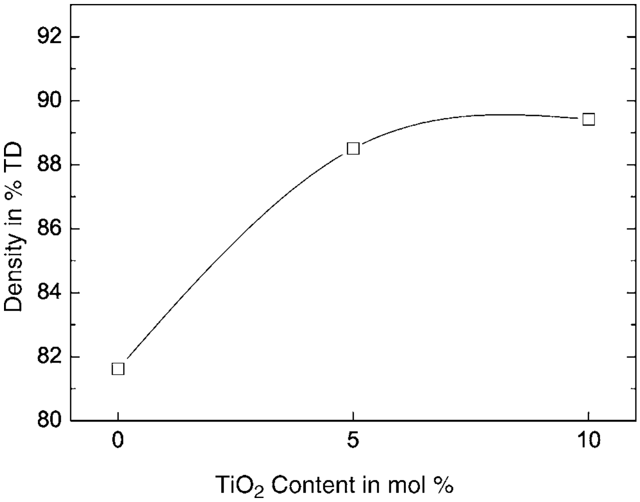

Fig. 2. Sintered density of the conventionally sintered Li_2TiO_3 pellets with various TiO_2 contents.

The addition of TiO_2 also results in a remarkable increase in the density during isothermal sintering. Fig. 2 shows the densities of the samples sintered at 1050 °C for 1 h in air. Since the sintering temperature is considerably lower than the eutectic temperature of the Li_2O–TiO_2 system [7], the possibility of liquid phase sintering due to excess TiO_2 can be excluded. In the absence of a liquid phase, an enhancement of the densification by the excess TiO_2 can be accounted for by one of two possible mechanisms [8]. Firstly, the excess TiO_2 may form point defects in the Li_2TiO_3 lattice and thereby increase the diffusivities. Secondly, the excess TiO_2 may significantly retard the grain growth or inhibit an abnormal grain growth so that the pores are linked to the grain boundaries.

Fig. 3 shows the results of the XRD analysis of the isothermally sintered Li_2TiO_3 pellets with various TiO_2 contents. The composition of the 5% TiO_2-doped Li_2TiO_3 is located near the TiO_2-rich phase boundary of β-Li_2TiO_3. A small amount of the excess TiO_2 appears to be form the $Li_4Ti_5O_{12}$ phase. Small peaks of $Li_4Ti_5O_{12}$ were observed in the TiO_2-doped samples

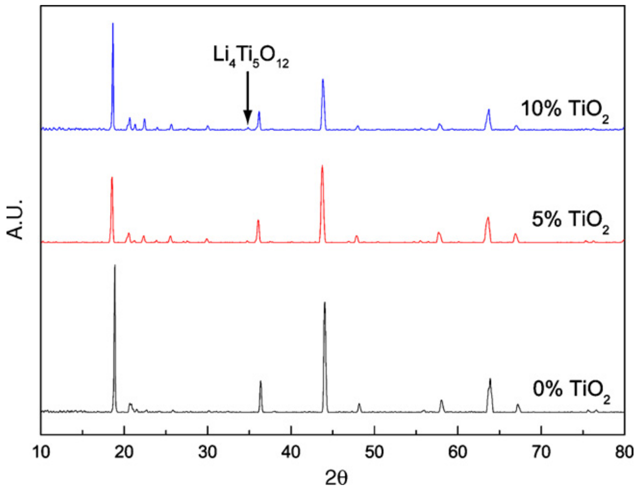

Fig. 3. X-ray diffraction patterns of sintered Li_2TiO_3 pellets with various TiO_2 contents.

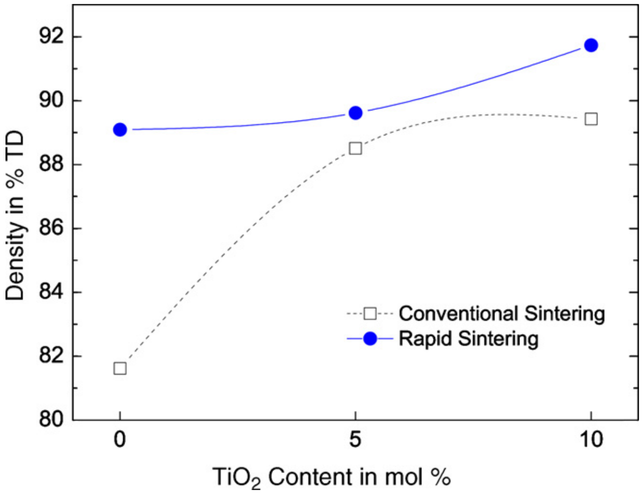

Fig. 4. Sintered density of the rapidly sintered Li_2TiO_3 pellets with various TiO_2 contents.

and the peak intensity of $Li_4Ti_5O_{12}$ became larger by increasing the excess TiO_2 content.

In order to increase the sintered density and to ensure a small grain size, the rapid sintering was conducted first in the Li_2TiO_3 system. The samples were rapidly heated to 1300 °C and then annealed at 1000 °C for 1 h in air. The heating and cooling rates of the rapid sintering were about 150 K/min. Solid line in Fig. 4 indicates the densities of the rapidly sintered undoped and TiO_2-doped Li_2TiO_3 pellets. Dashed line refers to the densities of the conventionally sintered pellets.

The rapidly sintered undoped Li_2TiO_3 sample has a very high density, around 89% of the theoretical density, without TiO_2 addition. This value is similar to those of the conventionally sintered TiO_2-doped Li_2TiO_3 samples. In the case of the TiO_2-doped Li_2TiO_3, the rapid sintering has little effect on the densification when compared with the conventionally sintered TiO_2-doped Li_2TiO_3. Usually, the activation energy of the densification is larger than that of the grain boundary motion. Therefore, an effective densification can be achieved by a rapid heat treatment at high temperature for short time. This result suggests that the rapid sintering appears to be a possible means of improving the sintered density of undoped Li_2TiO_3.

Fig. 5 shows the optical micrographs of the polished and etched surfaces of the conventionally and rapidly sintered Li_2TiO_3 pellets. The conventionally sintered samples in Fig. 5a–c have small grain sizes of about 4 μm, which seemed to be irrelevant to the TiO_2 contents. However, grain sizes of the rapidly sintered samples in Fig. 5d–f are larger than those of the conventionally sintered samples. They have grain sizes of about 12 μm for the undoped one and about 30 μm for the TiO_2-doped ones.

Rapid sintering in the Li_2TiO_3 system remarkably enhances the densification, especially for the undoped Li_2TiO_3. The rapid sintering schedule of the present investigation does not ensure a small grain size when compared with those of the conventionally sintered samples. However, even if the densities of the rapidly sintered samples have similar values among the undoped Li_2TiO_3 pellet and the TiO_2-doped Li_2TiO_3 pellets, the grain size of the undoped Li_2TiO_3 pellet is much smaller than those of the TiO_2-doped Li_2TiO_3 pellets. Rapid sintering appears to be a possible means of improving the densification of Li_2TiO_3 with preserving a small grain size.

Temperature dependence on the thermal diffusivity of the Li_2TiO_3 pellets is shown in Fig. 6. The thermal diffusivity

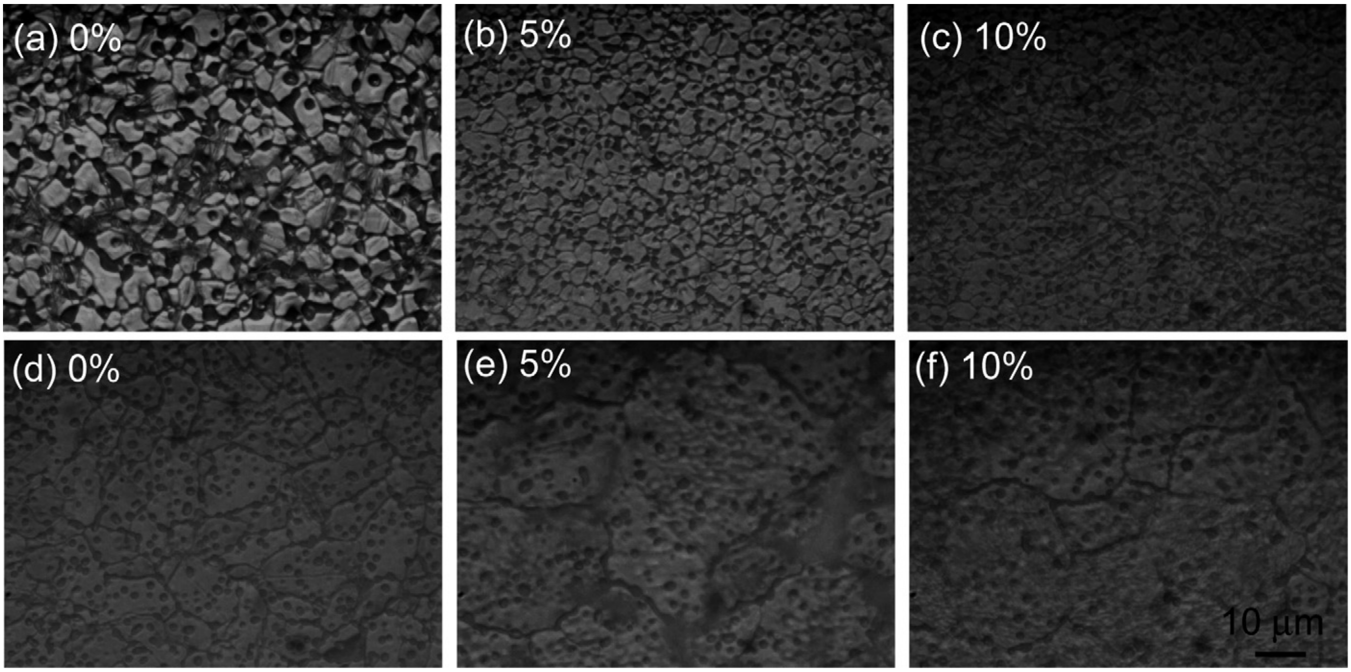

Fig. 5. Microstructures of the undoped and the TiO_2-doped Li_2TiO_3 pellets: (a–c) conventionally sintered at 1050 °C; (d–f) rapidly sintered at 1300 °C. Numbers indicate the contents of TiO_2 doping.

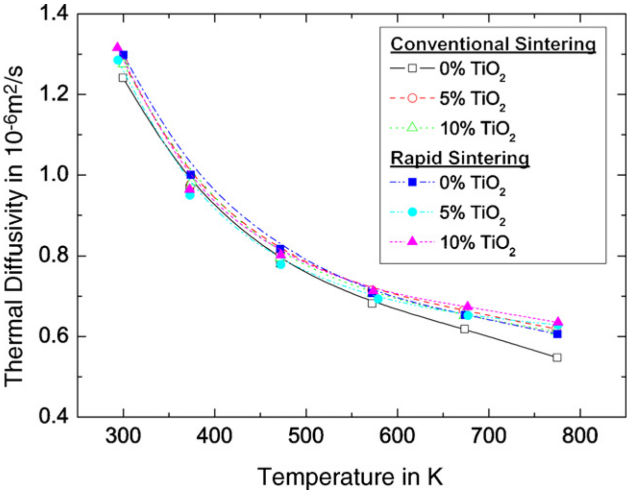

Fig. 6. Temperature dependence of thermal diffusivity of Li_2TiO_3.

decreased with the temperature from around 1.2×10^{-6} m^2/s at room temperature to about 0.6×10^{-6} m^2/s at 773 K. Only the conventionally sintered undoped Li_2TiO_3 pellet showed a slightly lower thermal diffusivity value for the whole temperature range. The others show similar values for the whole temperature range.

The lower thermal diffusivity of the conventionally sintered undoped Li_2TiO_3 pellet could be attributed to the lower density. Saito et al. [9] expressed the density dependence on the thermal conductivity by the modified Maxwell–Eucken equation. They also reported that the thermal diffusivity of the Li_2TiO_3 pellet decreased with increasing the porosity.

It appears that the content of the TiO_2 doping has little effect on the thermal diffusivity of the sintered Li_2TiO_3 pellets. The present finding is inconsistent with that of a previous study [10]. Hoshino et al. [10] compared the thermal diffusivity of a Li-deficient Li_2TiO_3 pellet with the literature values of a stoichiometric Li_2TiO_3 pellet [9,11]. They insisted that the thermal diffusivity of the nonstoichiometric Li_2TiO_3 pellet is higher than that of the stoichiometric Li_2TiO_3 pellet [10]. However, it seems that the processing variables might affect the thermal diffusivity of the Li_2TiO_3 pellet. By comparing the thermal diffusivity of the rapidly sintered undoped Li_2TiO_3 pellet with those of TiO_2-doped Li_2TiO_3 pellets, it appears to have similar thermal diffusivities for all the samples in Fig. 6.

4. Conclusion

The densification kinetics of TiO_2-doped samples were measured by using a push rod type dilatometer. Excess TiO_2 enhanced the shrinkage of the Li_2TiO_3 compacts and increased the sintered density considerably. The rapid sintering was conducted in an undoped Li_2TiO_3 system. The density of the rapidly sintered undoped Li_2TiO_3 pellet remarkably increased and it was similar to that of the TiO_2-doped Li_2TiO_3 pellet. The thermal diffusivity of the rapidly sintered undoped Li_2TiO_3 pellet also increased due to the enhanced densification. The present investigation suggests that the rapid sintering appears to be a possible means of improving the densification of Li_2TiO_3 with preserving a small grain size.

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