Effect of Excess TiO_2 and Heating Schedule on the Densification of Li_2TiO_3 Pellet

Young Woo Rhee, Kun Woo Song, Jong Hun Kim, Jae Ho Yang, Keon Sik Kim, Ki Won Kang, Yeon Ho Jung
Advanced PWR Fuel Development Team, KAERI, Daejon 305-
youngwoo@kaeri.re.kr

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 blanket of future fusion reactors. Li_2TiO_3 has been recently noticed as the leading candidate because of its prominent tritium release rate at low temperatures between 200 and 400 °C [1,2].

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

In this study, the densification kinetics of TiO_2 added Li_2TiO_3 were measured using a push rod type dilatometer. As a new attempt, the rapid sintering was conducted in order to increase the sintered density and to ensure small grain size.

2. Experimental

Samples of TiO_2 added Li_2TiO_3 were prepared from Li_2TiO_3 (Kosundo chemicals, 99.9% in purity) and TiO_2 (Degussa, 99.9% in purity) powders. The 0 mol%, 5 mol% and 10 mol% TiO_2-added 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 compacts were about 58 % of the theoretical density. The shrinkage behavior of 0 %, 5 % and 10 % TiO_2-added compacts in air was studied using a push rod type dilatometer (Netzsch, Dil402C).

For 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 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 at 1300 °C for 10 min and then annealed at 1000 °C for 1 h in air. The heating rate of 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 optical microscope and XRD, respectively.

3. Results

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

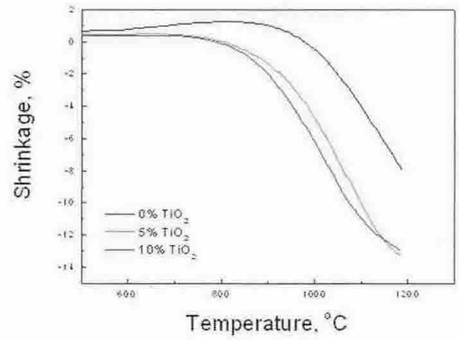

Figure 1. Shrinkage curves for TiO_2-added Li_2TiO_3 compacts.

The addition of TiO_2 also results in the remarkable increase in density during isothermal sintering. Figure 2 shows the densities of the samples sintered at 1050 °C for 1 h in air. Since the sintering temperature is well lower than the eutectic temperature of Li_2O-TiO_2 system [3], the possibility of liquid phase sintering due to excess TiO_2 can be excluded. In the absence of a liquid phase, the enhancement of densification by the excess TiO_2 can be accounted by one of the two possible mechanisms [4]. 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 abnormal grain growth so that pores are linked to the grain boundaries.

Figure 3 shows the results of XRD analysis of the isothermally sintered Li_2TiO_3 pellets with various TiO_2 contents. The composition of 5 % TiO_2-added Li_2TiO_3 is located near the TiO_2-rich phase boundary of β-Li_2TiO_3. The 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-added samples and the peak intensity of $Li_4Ti_5O_{12}$ became large with increasing the excess TiO_2 contents.

In order to increase the sintered density and to ensure small grain size, the rapid sintering was firstly conducted in Li_2TiO_3 system. Usually, the activation energy of the densification is larger than that of grain boundary motion. Therefore, effective densification can be achieved rapid heat treatment at high temperature for short time. The circle in Fig. 2 indicates the density of rapid-sintered 0 % TiO_2-added Li_2TiO_3. The sample was rapidly heated at 1300 °C for 10 min and then annealed at 1000 °C for 1 h in air. The heating and cooling rates of rapid sintering were about 150 K/min. The rapid-sintered sample has a very high density, around 91 % of theoretical density, without TiO_2 addition. This result suggests that the rapid sintering appears to be a possible means of improving the sintered density of Li_2TiO_3.

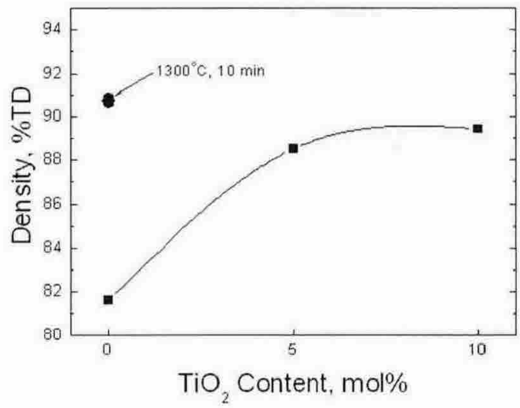

Figure 2. Sintered density of Li_2TiO_3 pellets with various TiO_2 contents.

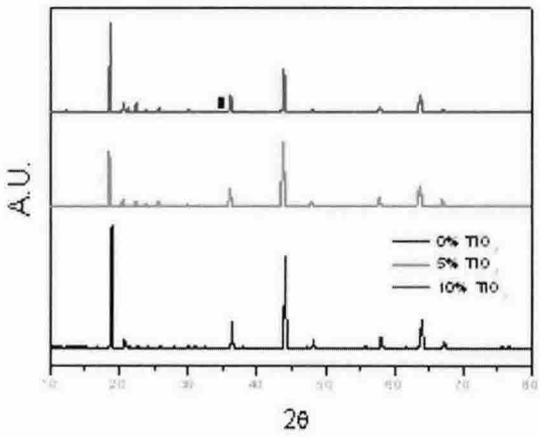

Figure 3. X-ray diffraction patterns of the sintered Li_2TiO_3 with various TiO_2 contents. Square indicates the peak of $Li_4Ti_5O_{12}$

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4. Conclusion

The densification kinetics of TiO_2 added samples were measured using a push rod type dilatometer. Excess TiO_2 enhance the shrinkage of Li_2TiO_3 compacts and increase the sintered density considerably. The rapid sintering was conducted in undoped Li_2TiO_3 system. The density of rapid-sintered undoped Li_2TiO_3 remarkably increased and is similar to that of TiO_2-added Li_2TiO_3.

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