Mass Transfer Behavior and Microstructure Evolution of Li4TiO4-Li2TiO3 Core-shell Breeding Ceramic Under Harsh Operating Conditions

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Abstract

The development of novel tritium breeding materials was urgently needed in order to continuously optimize the tritium breeding ratio (TBR) of thermonuclear fusion reactors. From this point of view, Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell breeding materials with more reasonable structure and theoretical Li density of 0.464 g/cm$^3$ were prepared in this work. Notably, the mass transfer experiment at 900 °C in 1% H$_2$/Ar shows that the theoretical Li density of this core-shell material after heating for 30 days was significantly higher than that of other breeding materials, indicating that it can provide more stable and efficient TBR. Specifically, the Li mass loss of the sample after 30 days heating was 3.4%, resulting in a decrease of Li density to 0.415 g/cm$^3$. The mechanism of Li mass loss in Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell breeding materials was investigated in detail. Moreover, the samples did not crack or collapse during the long-term heating process, and always maintained a satisfactory crushing load, revealing that this core-shell breeding ceramic can be used for a long time under severe operating conditions.

1. Introduction

With the continuous consumption of traditional fossil energy and the deterioration of climate and environmental problems, the development of a green and sustainable energy system is the current research focus [1, 2]. As a sustainable clean energy, fusion energy hopes to solve human energy problems once and for all [3]. To realize the fuel cycle of the fusion reactor, it is necessary to provide tritium through the nuclear reaction of tritium breeding materials and neutrons [4–8]. Li$_2$TiO$_3$ solid breeding ceramic is regarded as an ideal tritium breeding material due to its good chemical stability, reasonable irradiation stability and satisfactory tritium recovery at low temperatures [9–13]. However, researchers have found that the mass of Li$_2$TiO$_3$ will decrease over time in a H$_2$ atmosphere [14]. The loss of lithium content and the change of structure will affect the tritium breeding ratio (TBR), and it seems difficult to meet all the requirements for TBR by using only Li$_2$TiO$_3$ as breeder material. Further research found that adding Li$_4$TiO$_4$ to Li$_2$TiO$_3$ can not only improve the structural stability at high temperatures, but also increase the lithium density to a certain extent [15]. Moreover, it should be noted that Li$_4$TiO$_4$ is not stable in the air and easily reacts with CO$_2$ and moisture [16–18]. Inspired by the above research and aimed at suppressing the instability of Li$_4$TiO$_4$, an advanced Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell ceramic pebble was proposed in the previous study[19, 20]. In order to further increase the lithium density of the core-shell pebbles, it is necessary to further reduce the thickness of the Li$_2$TiO$_3$ shell without affecting the mechanical properties.

On the other hand, studying the mass transfer behavior of tritium breeding materials under operating conditions (1% H$_2$/Ar atmosphere at 900 °C) is a key issue for building a stable and safe fuel cycle. Due to the release of physically adsorbed water and chemically adsorbed water, as well as the reaction between O in the ceramic and H in the purge gas, the presence of water vapor under operating conditions cannot be ignored [21]. Many studies have shown that the presence of water vapor will have a dramatic effect on the form of tritium release, since tritium can be easily transferred into water vapor through
isotopic exchange reactions [22]. Furthermore, it has been demonstrated that the Li mass loss of breeding materials will be more severe in water vapor than in H\textsubscript{2} atmosphere [23]. Therefore, understanding the water vapor release behavior of tritium breeding materials is of great significance to predict and analyze the tritium release behavior. In addition, the volatilization of Li or Li-containing compounds is unavoidable at high temperature operating conditions [24]. Li mass loss is a key issue in establishing a self-sustaining tritium cycle. However, the experimental data and mechanism of water vapor release behavior and Li mass loss from Li\textsubscript{4}TiO\textsubscript{4}-Li\textsubscript{2}TiO\textsubscript{3} core-shell breeding materials are still unclear. At the same time, the structural evolution of the core-shell material in the long-term heating process is also worthy of attention.

In this work, Li\textsubscript{4}TiO\textsubscript{4}-Li\textsubscript{2}TiO\textsubscript{3} core-shell breeding ceramics with a thinner shell and higher theoretical lithium density were successfully prepared by the PVP-assisted granulation method. The water release behavior of this core-shell material in Ar and H\textsubscript{2} atmospheres, as well as the Li mass loss and structural changes caused by long-term heating in a H\textsubscript{2} atmosphere at 900°C have been studied in detail.

2. Experimental Section

2.1 Materials Preparation

The preparation process of Li\textsubscript{4}TiO\textsubscript{4}-Li\textsubscript{2}TiO\textsubscript{3} core-shell pebbles was a further optimization of the previously reported granulation method [20]. Firstly, Li\textsubscript{4}TiO\textsubscript{4} and Li\textsubscript{2}TiO\textsubscript{3} precursor powders were synthesized by solid-phase reaction. Subsequently, these precursor powders were preheated at 750 °C and 500 °C to obtain Li\textsubscript{4}TiO\textsubscript{4} and Li\textsubscript{2}TiO\textsubscript{3} powders for granulation. Different from the previous study in which the powder was wrapped in a PVP layer and then sprayed with water mist for granulation, this study uses a simpler PVB (polyvinyl butyral) system. That was, 0.1 g of PVP was added to 100 ml of 50 °C absolute ethanol and stirred for 1 h to obtain the 0.1wt.% PVP solution. Then, 0.2 ml of PVB solution was sprayed on the surface of 1.0 g of Li\textsubscript{4}TiO\textsubscript{4} powder followed by a rolling mix at 200 rpm for 1 min. The Li\textsubscript{4}TiO\textsubscript{4} spherical core with a diameter of ~ 1 mm can be obtained by repeating the above steps about 10 times. After that, just change the powder to Li\textsubscript{2}TiO\textsubscript{3} and continue to repeat the above steps until the pebbles grow to ~1.4 mm to obtain the core-shell green body. Finally, the Li\textsubscript{4}TiO\textsubscript{4}-Li\textsubscript{2}TiO\textsubscript{3} core-shell ceramic pebbles were obtained by sintering the green body at 900 °C in vacuum.

2.2 Water vapor release and mass loss experiment

The schematic diagram of the equipment for the water vapor release behavior experiment was shown in Fig. 1. Before the experiment, 0.3 g of Li\textsubscript{4}TiO\textsubscript{4}-Li\textsubscript{2}TiO\textsubscript{3} core-shell samples were fixed in the center of a quartz tube with a diameter of 4 mm through quartz wools. Ar and H\textsubscript{2}/Ar gas were used as purge gas respectively, and the concentration of hydrogen in the mixed gas was 10000 ppm. The flow rate of purge gas was controlled at 400 cc/min by mass flow controller, and the residual moisture in the gas was removed by Molecular Sieves 5A bed (MS-5A). Moreover, the concentration of water vapor released during the experiment is monitored by a hygrometer (MAH-50, SHIMAZU Co.).
At the beginning of the experiment, Ar was introduced at room temperature to remove the physically adsorbed water in the sample and pipe. Subsequently, the sample bed was heated to 500 °C to release the chemically adsorbed water, and then H₂/Ar was introduced and heated to 900 °C to release the generated water. It was worth noting that two different heating methods are used to achieve different purposes. One was a continuous heating method that maintains a heating rate of 5 °C/min, and the other was a stepwise heating method with an interval of 100 °C.

For the mass loss experiment, the sample bed was heated at 900 °C in H₂/Ar atmosphere for 3 days, 10 days and 30 days, and the mass changes before and after the experiment were recorded. Without considering the amount of CO₂ adsorbed on the sample surface, the Li mass loss was calculated by Eq. (1) [25].

\[
\text{Li mass loss} = \text{Sample weight before heating} - \text{Sample weight after heating} - \text{Weight of physical adsorption water and chemical adsorption water} - \text{Weight of O released as generated water vapor}
\]

2.3 Characterization

The morphology and microstructure of the sample before and after heating are observed by a field-emission scanning electron microscope (SEM, Model S-4800, Hitachi, Japan). The particle size of the sample was counted and calculated using the Nano Measure software. The weight of the sample was measured by an electronic balance with an accuracy of 0.0001 g. In addition, the specific surface area of the sample was measured by a micrometric automatic surface analyzer (TriStar-II3020, SHIMAZU Co.) based on N₂ gas adsorption method.

The crush load of Li₄TiO₄-Li₂TiO₃ core-shell ceramic with different heating times was measured by a universal material testing machine (SHIMADZUAG-IC). Each group of samples measured 10 pebbles and calculated the average value and standard deviation.

3. Result And Discussion

Fig. 2(a-d) shows the optical photograph and SEM morphology of the Li₄TiO₄-Li₂TiO₃ core-shell ceramic pebbles prepared by the optimized granulation method and sintered at 900 °C. As we can see, the as-prepared ceramic pebbles are light yellow and have a relatively uniform size distribution (Fig. 2(a)). Since the cross-section of the pebble is obtained by physical destruction, it is difficult to obtain a complete hemispherical section. However, it can also be seen from Fig. 2(c) that the core-shell pebble is composed
of a relatively loose Li₄TiO₄ core with a diameter of ~950 μm and a dense Li₂TiO₃ shell with a thickness of ~160 μm. In addition, the grain sizes of Li₄TiO₄ and Li₂TiO₃ particles are 1.5±0.2 μm and 0.4±0.1 μm, respectively (Fig. 2(b) and (d)).

For the water vapor release behavior at a constant heating rate of 5 °C/min, Fig. 3(a) presents the water vapor release curve of Li₄TiO₄-Li₂TiO₃ core-shell pebbles. It can be seen that the peak 1 released at room temperature corresponds to the physically adsorbed water in the sample. When the sample bed starts to heat up, the three peaks (peak 2-4) appearing earlier correspond to the chemically adsorbed water in the sample. As the temperature further increased, the release peak (peak 6) corresponding to high-temperature generated water appears, and the maximum peak value is 688 ppm. Since the data on the water vapor release behavior of Li₄TiO₄ has never been studied, for comparative analysis with the core-shell pebbles, we used the same granulation method to prepare Li₄TiO₄ pure phase pebble and used 0.3 g of this sample to conduct water vapor release experiments. As shown in the results from Fig. 3(b), the water vapor release trend of Li₄TiO₄ pebbles is basically the same as that of core-shell pebbles, but the amount of physically adsorbed water and chemically adsorbed water is slightly higher. Remarkably, the peak value of high temperature generated water of Li₄TiO₄ is 1883 ppm, which is much higher than that of core-shell pebble. The main reason for this difference may be that the oxygen activation site concentration of Li₄TiO₄ is much higher than that of Li₂TiO₃ [21]. Furthermore, the specific surface area of core-shell pebbles and Li₄TiO₄ pebbles are measured as 0.75 m²/g and 1.30 m²/g, respectively. The higher specific surface area may also be the cause of this phenomenon.

It cannot be ignored that the peak 5 in Fig. 3 at around 600 °C is difficult to classify as chemically adsorbed water or generated water. This requires a comprehensive judgment based on the corresponding water release at each temperature under stepwise heating. Fig. 4(a) and (b) show the chemical adsorbed water release curves of core-shell pebbles and Li₄TiO₄ pebbles under stepwise heating, respectively. It can be inferred that the water release peaks at 100 °C, 200 °C, and 300 °C correspond to peak 2, peak 3, and peak 4 in Fig. 3. Besides, the lower water release peak at 500 °C indicates that the chemical adsorbed water of these two materials can be removed before 500 °C. It can be seen from Fig. 4(c) and (d) that the generated water release peaks at 600 °C and 700 °C correspond to peak 5 and peak 6 in Fig. 3. It should be noted that there are more overlaps between peak 4 and peak 5 of core-shell pebbles in Fig. 3, revealing that the Li₂TiO₃ shell may inhibit the water release rate of Li₄TiO₄ core.

Since the desorption of chemical adsorbed water and the formation of water at high temperatures are mainly reactions on the surface of the crystal grains, it is important to study the release capacity of chemical adsorbed water and generated water per unit surface area. Among them, the release amount of chemical adsorbed water or generated water at each temperature can be calculated by Eq. (2).

\[
n(\text{mol}) = \frac{\text{Area} \times 10^{-6} \times 0.4 \times \text{Flow rate (L/sec)}}{R \times 300 \times \text{[Gas Temp.]}}
\]  

(2)
where \( n \), Area and R were the amount of water released, area of the water release curve at each temperature in Fig. 3 and gas constant. Finally, the amount of chemical absorbed water and generated water per unit surface area for various ceramic breeder materials are shown in Fig. 5 [21,22,26–28]. It can be seen from Fig. 5(a) that the amount of chemical adsorbed water per unit specific surface area of core-shell pebbles and \( \text{Li}_4\text{TiO}_4 \) pebbles is very close, and both are higher than most breeding materials. The relatively flat curve reveals that the difference in the amount of water vapor released at each temperature is small. On the other hand, the amount of generated water per unit specific surface area of core-shell pebbles and \( \text{Li}_4\text{TiO}_4 \) pebbles is only lower than that of \( \text{Li}_2\text{TiO}_3 \) (JAEA) (Fig. 5(b)). The trends of the two curves are completely consistent, indicating that the water vapor release behavior of the core-shell pebble is mainly affected by the \( \text{Li}_4\text{TiO}_4 \) core. Given the above, compared with other breeding materials, core-shell pebbles and \( \text{Li}_4\text{TiO}_4 \) pebbles have a higher water release amount, which may lead to an increase in the proportion of HTO during the tritium release of these materials.

For the long-term heating test, it can be seen from Fig. 6 that with the extension of the heating time, the color of the \( \text{Li}_4\text{TiO}_4\text{-Li}_2\text{TiO}_3 \) core-shell pebble gradually changes from light yellow to brown. This is mainly because during the heating process, the H in the purge gas will react with the O in the ceramic, and the detachment of O will cause the formation of oxygen vacancies in the ceramic, resulting in a darker color of the material. In addition, we also found that obvious white deposits can be observed at the end of the quartz tube after 30 days of heating, which is caused by the redeposition of lithium. Previous studies have shown that this white deposit is mainly composed of \( \text{Li}_2\text{SiO}_3 \) [29]. The Li mass loss of \( \text{Li}_4\text{TiO}_4\text{-Li}_2\text{TiO}_3 \) core-shell pebbles over time is shown in Fig. 7. It can be seen that the Li mass loss caused by heating for 3 days, 10 days and 30 days is 1.2 %, 2.9 % and 3.4 % respectively. And the Li mass loss rate was the fastest in the first three days, then the rate gradually decreased and became relatively flat after 10 days. According to the above results, a schematic diagram of Li vaporization in the quartz tube can be concluded as shown in Fig. 8. In general, the mass loss of Li in breeding material is considered to be volatilized as the basic unit of \( \text{Li}_2\text{O} \) [30,31]. Due to the release of chemical adsorbed water and generated water during the early heating process, there is a certain concentration of water vapor in the sample bed, which will react with \( \text{Li}_2\text{O} \) in the breeding material to form \( \text{LiOH} \) (Eq. (3)).

\[
\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{LiOH}
\]

Since the volatilization temperature of \( \text{LiOH} \) is much lower than that of \( \text{Li}_2\text{O} \), it will cause Li mass loss at a faster rate in the initial heating stage. Then, the water vapor concentration in the sample bed will gradually decrease with the heating time, resulting in a decrease in the proportion of \( \text{LiOH} \) in the volatiles, so the rate of Li mass loss will slow down. When the water vapor in the sample is completely removed, the mass loss of Li in the material changes into simple \( \text{Li}_2\text{O} \) volatilization, resulting in a relatively slow volatilization rate.

As an important parameter affecting TRB, Li density is a reliable basis for evaluating the performance of breeding materials. In particular, the reduction of Li density caused by long-term heating...
under operating conditions has always been a research hotspot in the field of breeding materials. For this reason, we will comparatively study the evolution of Li density with heating time in a 900 °C H$_2$/Ar atmosphere of core-shell pebbles and other breeding materials [32,33]. In order to be unified with other studies, the theoretical lithium density is used for comparison. The theoretical Li density of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles is calculated by Eq. (4).

\[
\rho_{Li} = \frac{V_{core} \times \rho_{Li_4TiO_4} \times \omega_{Li_4} + V_{shell} \times \rho_{Li_2TiO_3} \times \omega_{Li_2}}{V_{shell} + V_{core}}
\] (4)

Where $\rho_{Li}$, $V_{core}$, $V_{shell}$, $\rho_{Li_4TiO_4}$, $\rho_{Li_2TiO_3}$, $\omega_{Li_4}$ and $\omega_{Li_2}$ were theoretical Li density, core volume, shell volume, density of Li$_4$TiO$_4$, density of Li$_2$TiO$_3$, mass fraction of Li in Li$_4$TiO$_4$ and mass fraction of Li in Li$_2$TiO$_3$. The initial theoretical Li density of the core-shell material is calculated to be 0.464 g/cm$^3$. Fig. 9 presents the evolution of the Li density of various breeding materials overtime during the heating process. It can be seen that after 30 days of heating, the theoretical Li density of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles decreased from 0.464 g/cm$^3$ to 0.415 g/cm$^3$. More interestingly, during the first 10 days of heating, the theoretical Li density of the core-shell pebbles was significantly lower than those of Li$_8$ZrO$_6$, β-Li$_5$AlO$_4$-Li$_8$ZrO$_6$ and β-Li$_5$AlO$_4$. However, in the subsequent heating process, the theoretical Li density of core-shell pebbles can always be maintained at a high level, and is significantly higher than most breeding materials at 30 days. This is mainly because the different structures of this core-shell pebbles play different roles, that is, the Li$_4$TiO$_4$ core increases the Li density while suppressing its instability through the Li$_2$TiO$_3$ shell. It also reveals that this advanced core-shell breeding material can maintain satisfactory thermal stability during long-term heating.

Since tritium breeding materials need to be used in the blanket for a long time, the problems of material deformation and grain growth caused by long-term heating have attracted the attention of researchers. However, due to the strict requirements of the experiment on equipment and technology, there are few reports about the microstructure changes caused by long-term heating under H$_2$ purge gas, let alone the 30 days. Moreover, different from the traditional tritium breeding materials, the core-shell structure tritium breeding materials should not only pay attention to the grain growth in the long-term heating process, but also consider the bonding problem at the interface between the core and the shell. Figure. 10 shows the evolution of the overall morphology of the core-shell pebbles with heating time. It can be observed that as the heating time increases, the surface of the core-shell pebble always maintains a complete structure without obvious cracks and defects, revealing that this core-shell ceramic has satisfactory thermodynamic stability (Fig. 10(a-d)). Further observation of the cross-sectional morphology shows that the gap between the core and the shell in the sample gradually increases with the increase of heating time (Fig. 10(e-h)). It is worth noting that the difference in Li evaporation rate and grain growth rate in Li$_4$TiO$_4$ core and Li$_2$TiO$_3$ shell will cause this phenomenon, which needs to be judged by the evolution of microstructure.
The microstructure of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles after 3 days, 10 days and 30 days heating is shown in Fig. 11(a-f). Compared with the initial microstructure of this material in Fig. 2, its microstructure has changed significantly after 3 days of heating. After heating for 3 days, the grain size of the Li$_2$TiO$_3$ shell grows from 0.4±0.1 μm to 2.5±0.5 μm, and the grain size of Li$_4$TiO$_4$ core grows from 1.5±0.2 μm to 3.3±1.0 μm. It is also found that the grain structure in the Li$_2$TiO$_3$ shell is relatively uniform and angular, while the grain structure in the Li$_4$TiO$_4$ core is more diverse and relatively rounded. Continue heating to 10 days and 30 days, the grain size in the shell further grows to 4.1±1.1 μm and 6.5±1.5 μm, and the grain size in the core further grows to 4.7±1.3 μm and 6.9±2.5 μm. According to Eq. (5), it is not difficult to judge that the grain size will directly affect the specific surface area [34].

$$A_{BET} = \frac{6}{d \rho}$$  (5)

where d is the grain diameter and $\rho$ is the theoretical density of grain. In order to more clearly show the change in specific surface area caused by the change in grain size with heating time, the relevant results are presented in Fig. 12. Obviously, the specific surface area of the core-shell pebbles keeps decreasing as the grain size increases. And the specific surface area of the sample decreased from 0.75 m$^2$/g to 0.08 m$^2$/g after heating for 30 days. Furthermore, similar to the evolution trend of grain size, the change rate of the specific surface area in the first three days is also the fastest, and then it gradually slows down. In addition, we can also observe that the grain growth rate in the core-shell is basically consistent, which also confirms that the gap between the core and the shell is caused by the difference of Li evaporation rate, that is, the Li evaporation rate of Li$_4$TiO$_4$ is higher than that of Li$_2$TiO$_3$.

It is well known that the grain size of breeding materials has a significant effect on the tritium release behavior. An excessively large grain size will increase the migration path of tritium in the bulk of grain and reduce the diffusion path of tritium between the grains, which is not conducive to the rapid tritium release. Therefore, the ideal grain size should be less than 5 μm [35]. On the other hand, surface desorption also plays an important role in the tritium release behavior [36]. The reduction of the specific surface area caused by the grain growth will lead to the reduction of the number of surface-active sites for desorption. And eventually leads to a slower surface desorption rate or higher surface desorption temperature. From this point of view, the change of grain size and specific surface area of the core-shell breeding material after long-term heating may lead to a slower tritium release rate or a higher tritium release temperature.

Considering that breeding ceramic need to achieve high-density accumulation in blanket, and the debris formed by cracking during long-term service may block the equipment pipeline, posing a serious safety hazard. Therefore, the design requirements of the tritium breeding material need its crushing load ≥20 N [37,38]. Moreover, the research on the crushing load evolution of tritium breeding material with core-shell structure during long-term heating is still blank. For this reason, the effect of heating time on the crushing load of core-shell pebbles is shown in Fig. 13. The results show that the crushing loads of the core-shell pebbles after heating for 0 days, 3 days, 10 days and 30 days are 46.84±3.55 N, 49.41±6.71 N, 49.41±6.71 N,
27.79±5.36 N and 32.45±6.08 N, respectively. The reason for this phenomenon needs to be comprehensively analyzed in combination with the structural evolution and the crushing curve.

As shown in Fig.14(a), the crushing curve of as-received core-shell pebble shows only one fracture peak, indicating that the core and the shell are tightly bonded without any faults. In addition to the main fracture peak, the crushing curve of the core-shell pebble heated for 3 days also has a step value on its right side (Fig.14(b)). It reveals that there is a certain gap between the core and the shell at this time, which leads to the discontinuity of the crushing process, resulting in a step value. However, most positions of the core and shell interface are still tightly bonded, and the crushing load is increased due to factors such as the fusion and growth of crystal grains after long-time heating. The heating time was further extended to 10 days, and it was found that in addition to the main fracture peak, there were 1-2 lower fracture peaks (Fig.14(c)). Multiple independent fracture peaks indicate that the core-shell pebbles heated for 10 days have multiple fracture points during the crushing process, and the position interval between the peaks increases, indicating that the gap between the core-shell increases. We roughly think that the main fracture peak only represents the crushing load of the shell, which leads to a decrease in the crushing load of the whole pebble. The crushing curve of the core-shell pebble heated for 30 days is shown in Fig. 14(d). It can be seen that the core-shell gap is enlarged due to the volatilization of lithium under long-term heating, resulting in more fracture points detected during the crushing process. However, it can be seen from the value of the main fracture peak that the crushing load of the shell is further increased under the promotion of long-term heating. In general, although the crushing load of the pebbles fluctuates due to the grain growth and the change of the core-shell interface during the long-term heating process, the crushing load of the sample is always greater than the design requirement of 20 N for tritium breeding materials, and the sample always maintains good structural integrity during the heating process. Therefore, we believe that this Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles can be used for a long time under severe operating conditions.

4. Conclusions

In summary, this work is dedicated to studying the mass transfer and microstructure evolution of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles under operating conditions, to verify the possibility of using this material as a tritium breeding material. The phenomena observed in the two different heating methods indicate that the water vapor release behavior of Li$_4$TiO$_4$ in the core-shell pebble dominates the overall water vapor release trend, although the Li$_2$TiO$_3$ shell can slow down the water vapor release rate of the Li$_4$TiO$_4$ core to a certain extent. In addition, the amount of generated water per unit surface area of the core-shell pebbles is higher than that of most breeding materials, which may lead to an increase in the proportion of tritiated water in the tritium release process. For the long-term heating experiment, the Li mass loss rate was the fastest in the first three days, then the rate gradually decreased and became relatively flat after 10 days. The concentration of water vapor in the sample bed will directly determine whether the vaporization form of Li is mainly LiOH or Li$_2$O, thereby affecting the rate of Li mass loss. Compared with other breeding materials, the core-shell pebble can still maintain a higher Li density after heating for 30 days. Besides,
the evolution of morphology, microstructure, and crushing load reveals that the core-shell breeding ceramics have satisfactory thermodynamic stability and can be used for a long time under severe operating conditions.

**Declarations**

**Conflicts of interest**

There are no conflicts to declare.

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**Figures**
Figure 1

Schematic diagram of experimental equipment.

Figure 2

Optical picture and SEM cross-sectional morphology of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell ceramic pebbles: (a) optical picture, (b) Li$_4$TiO$_4$ core, (c) cross-section and (d) Li$_2$TiO$_3$ shell.
Figure 3

The release curves of water vapor from (a) Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell ceramic pebbles and (b) Li$_4$TiO$_4$ pebbles at a heating rate of 5 °C/min.

Figure 4
The release curves of water vapor from (a, c) Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell ceramic pebbles and (b, d) Li$_4$TiO$_4$ pebbles at a stepwise heating.

Figure 5

The amount of (a) chemical absorbed water and (b) generated water per unit surface area for various ceramic breeder materials.

Figure 6

Optical picture of the core-shell pebbles sample bed after heating for 30 days.
Figure 7

Normalized weight change with heating time (Mass loss takes Li$_2$O as the basic unit).
Figure 8

Schematic diagram of lithium vaporization.

Figure 9

Graph showing lithium density (g/cm$^3$) vs. heating time (day) with various markers and lines representing different materials and sources as indicated.
The evolution of the theoretical Li density of various breeding materials over time during the heating process.

Figure 10

Evolution of SEM morphology of $\text{Li}_4\text{TiO}_4$-$\text{Li}_2\text{TiO}_3$ core-shell ceramic pebbles with heating time: (a-d) surface and (e-h) cross section.
Figure 11
Evolution of SEM microstructure of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell ceramic pebbles with heating time: (a-c) Li$_2$TiO$_3$ shell and (d-f) Li$_4$TiO$_4$ core.

Figure 12
Effect of heating time on grain size and specific surface area of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles.
Figure 13

Evolution of crushing load of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebbles with heating time.

Figure 14

Crushing load curve of Li$_4$TiO$_4$-Li$_2$TiO$_3$ core-shell pebble with different heating time: (a) as-received, (b) 3 days, (c) 10 days and (d) 30 days.