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Effects of multi-ion irradiation on microstructural changes in lithium titanate

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A B S T R A C T

The irradiation behavior of Li_2TiO_3 under a fusion reactor environment was simulated by simultaneous irradiation of Li_2TiO_3 by the triple ion beams and the respective single ion beams of O^{2+}, He^+ and H^+. The microstructural changes in Li_2TiO_3 caused by the irradiation were measured by FT-IR photoacoustic spectroscopy. The results suggest that the amount of TiO_2 formed is proportional to the dpa and that the method of irradiation does not affect the dependence of formation of TiO_2. On the other hand, the amount of defects and/or radiolytic products generated by irradiation, which is considered to trap hydrogen near the surface, is found to be affected by the method of irradiation. Such phenomena are believed to affect the tritium release behavior from Li_2TiO_3, and durability of Li_2TiO_3 and compatibility of Li_2TiO_3 with other components of the breeder blanket such as structural materials in the fusion reactor system under operation.

1. Introduction

The Li_2TiO_3 ceramic is one of the most suitable candidate solid breeder materials for D–T fusion reactors because of its low activation, excellent tritium migration and chemical stability [1–3]. In the fusion reactor environment irradiation damage will be caused by fast neutrons, energetic tritons (2.7 MeV) and helium ions (2.1 MeV) generated in $^6Li(n,\alpha)^3H$ reaction. The irradiation damage will result in microstructural changes that may affect the characteristics of the breeding materials, especially the tritium release behavior, compatibility with other materials, and so on [4]. Thus the study of irradiation defects and microstructural change caused by irradiation in Li_2TiO_3 is essential to evaluate its irradiation performance in a fusion reactor blanket.

Simulation of the fusion reactor environment and hence the study of any synergistic effects of atomic displacement damage in Li_2TiO_3 could be achieved with simultaneous irradiation with 'triple' ion beams, which consist of O^{2+}, He^+ and H^+. By using O^{2+} ion beam instead of fast neutrons, the generation rate of irradiation defects in Li_2TiO_3 is accelerated more than a thousand times. This means that the necessary amount of defects for the simulation can be generated within hours of the irradiation. In the previous study [5,6], the formation of TiO_2 layer on the surface of Li_2TiO_3 by irradiation with triple ions has been found. From comparison with the results of single beam irradiation of O^{2+}, He^+ and H^+, it was found that the amount of the formed TiO_2 was strongly affected by the radiation dose in displacement per atom (dpa). This suggests that the formation was mainly caused by the effect of knock on with respective ion beam irradiation. In addition, the defects and/or radiolytic products generated by irradiation would trap hydrogen near the surface. In the present study, the results of the FT-IR photoacoustic spectroscopy (PAS) with Li_2TiO_3 samples irradiated with the single beams, with the triple ion beams simultaneously and with the triple ion beams sequentially were analyzed to study the relation between the irradiation effects and the microstructural change.

2. Experimental

Li_2TiO_3 ceramics used in this experiment were fabricated from 99% pure powder purchased from CERAC, Inc. The powder was cold pressed at 300 MPa into cylinders, and subsequently sintered at 1223 K for 6 h in an Ar atmosphere. The resulting Li_2TiO_3 ceramics have approximately 78% theoretical density. The specimens were machined from the cylinders in the form of disks with diameter of 10 mm and thickness of 0.5–1 mm.

The Li_2TiO_3 samples were irradiated at 573 K with the triple ion beams and with single ion beams of 2.4 MeV O^{2+}, 0.6 MeV He^+ and 0.25 MeV H^+ in the triple beam irradiation facility in Takasaki laboratory of Japan Atomic Energy Research Institute [7]. The temperature of the samples was maintained at constant value during irradiation by using automatic temperature controller. The fluence range of the respective ions was from 3×10^{20} to 1×10^{21} ions/m^2. By considering the incident angle of each beams individually, the ion beam energies were determined by estimation with the TRIM code [8] to adjust the projected ranges of each species at about 2 μm. For estimating the effects of simultaneous multi-ion beams irradiation, simultaneous and sequential irradiation of the three kinds of ion beams were performed.

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Using the FT-IR photoacoustic spectroscopy (PAS) technique, the non-irradiated sample, the samples irradiated with the triple ion beam and the samples irradiated by the single ion beams were examined to obtain information near the end of the ion range. The photoacoustic signal was generated from the surface layers of the sample with a thickness of some micrometers, which is a function of the mirror velocity of the FT-IR interferometer and wave number. In this case, the mirror velocity was 2 cm/s that corresponds to the thickness of about 15–5 μm for 400–4000 cm^{-1}, so that the spectra of irradiated samples are a superposition of spectra of irradiated and non-irradiated zones of the sample.

3. Results and discussion

The FT-IR PAS spectrum of a non-irradiated sample is shown in Fig. 1 [6]. For comparison, the spectrum of irradiated sample with the triple ion beam is also shown in the figure. The characteristic peaks in FT-IR PAS spectra were observed around 680, 780, 880, 1090, 1430, 1480, 1570, 3150 and 3450 cm^{-1}. The 880, 1090, 1430 and 1490 cm^{-1} peaks are believed to be attributed to Li_2CO_3 which is one of the raw materials of Li_2TiO_3 samples and is believed to exist as an impurity in the samples [9]. In comparison to the reported spectra of TiO_2 and Li_2TiO_3, 680 and 780 cm^{-1} peaks are identified as due to Ti-O, and 1570, 3150 and 3450 cm^{-1} peaks are from the O-H bond in hydroxyls adsorbed on or near the surface [10–12].

Among the observed peaks, irradiation effect is clearly found for 780 and 3450 cm^{-1} peaks. Fig. 2 shows the relation between dpa and the 780 cm^{-1} peak area from the Ti–O bond, for each irradiation. The dpa was estimated with the TRIM code. It is shown that the peak area increases in proportional to the dpa, and any difference is not observed in the dependence of the peak area on dpa among the single, the simultaneous triple and the sequential triple ion beams irradiation, as shown in Fig. 2.

From the results of FT-IR PAS measurements using Li_2TiO_3 samples doped with 1–10% TiO_2, which simulate the formation of TiO_2 in Li_2TiO_3, it was shown that the 780 cm^{-1} peak area increases in proportion to the ratio of doped TiO_2 [6]. Therefore, the results shown in Fig. 2 suggest that TiO_2 is formed by the ion beam irradiation in Li_2TiO_3, and the amount of TiO_2 is proportional to the dpa in the samples. It means that the amount of TiO_2 formed by irradiation is strongly affected only by the dpa in the samples and independent on the method of irradiation, that is, single, simultaneous triple or sequential triple irradiation. In the previous study, it was found that the formation of TiO_2 is promoted by increase of the irradiation temperature [5]. Since the irradiation temperature in this study, 573 K, is much lower than the operation temperature of fusion reactor blanket, it is expected that the amount of TiO_2 formed in the blanket is larger than that observed in this study.

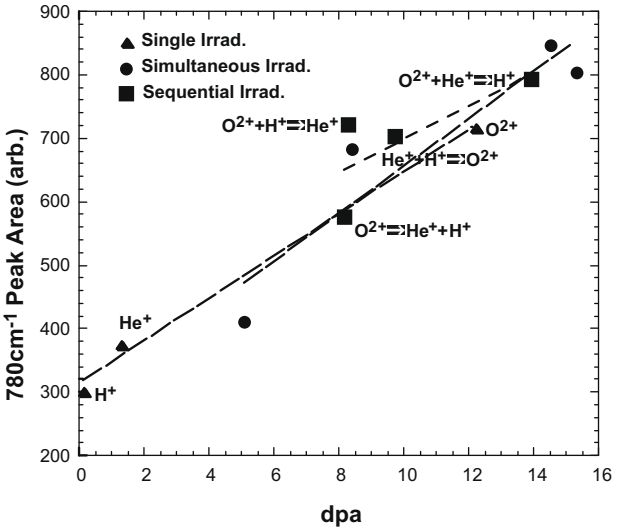

Fig. 2. Dependence of the 780 cm^{-1} peak area on dpa.

Fig. 3 shows the relation between the dpa and the 3450 cm^{-1} peak area, which is due to the O–H bond. The existence of this peak suggests the presence of hydroxyl group on or near the sample surface, which is considered to be generated by adsorption of water in the atmosphere during the experiment and the measurement. In this case, there is no relation between the increase of 3450 cm^{-1} peak area and the amount of doped TiO_2. Thus, it suggests that the increase of 3450 cm^{-1} peak area observed in the irradiation samples has no relation to the formation of TiO_2 by irradiation [6]. As shown in Fig. 3, for the single irradiation (filled triangles

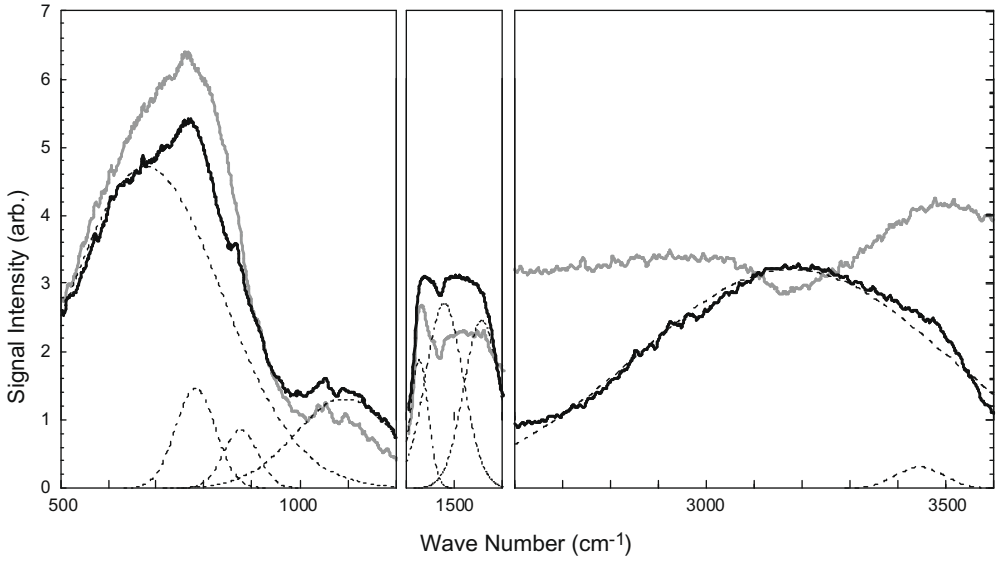

Fig. 1. FT-IR PAS spectrum of non-irradiated Li_2TiO_3 sample. Dashed lines are the results of peak analysis. The spectrum of irradiated sample with triple ion beam is also shown in gray lines for comparison.

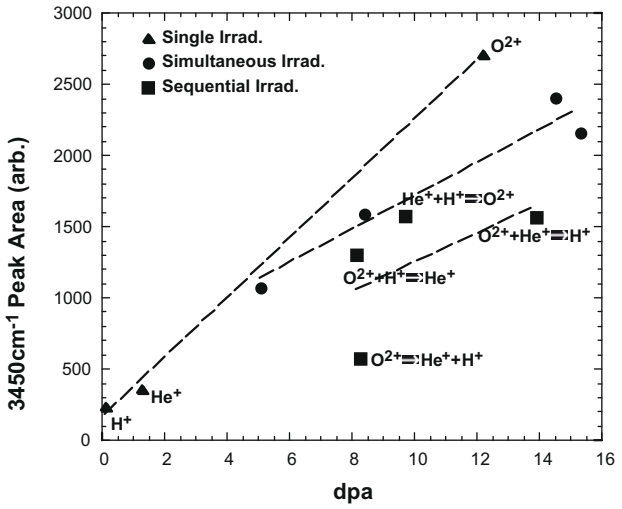

Fig. 3. Dependence of the 3450 cm^{-1} peak area on dpa. Notation for the sequential irradiation as 'A → B' means that irradiation of beam B was performed after closing of irradiation of beam A.

in the figure) and the simultaneous triple irradiation (filled circles in the figure), the peak area increases proportionally to the dpa, respectively. However, the increase of the peak area for the simultaneous triple irradiation seems to be smaller than that for the single irradiation. It is suggested that the generation of defects and/or radiolytic products, which are the trapping sites for hydrogen adsorbed on or near the surface, is strongly affected by displacements with such irradiation, but the generation rate of the trapping sites is different between the single irradiation and simultaneous triple irradiation.

For the sequential triple irradiation (filled squares in the figure), the peak area for the samples which irradiated with O^{2+} after simultaneous dual irradiation of He^+ and H^+, and with He^+ after simultaneous dual irradiation of O^{2+} and H^+ seems to have similar dependence on dpa to that for the case of simultaneous triple ion beams. On the other hand, increase of the peak area in the samples irradiated with H^+ after simultaneous dual irradiation of He^+ and O^{2+}, and with He^+ and H^+ simultaneously after O^{2+} irradiation seems to be smaller than that for the simultaneous triple irradiation samples.

These differences of dependence on dpa appeared due to the types of irradiation (single, simultaneous triple and sequential triple) are considered to be correlated with the relation between O^{2+} and H^+ irradiation. In the case that H^+ irradiation was performed simultaneously with or prior to O^{2+} irradiation, the increase of the peak area is degraded in comparison with the single irradiation, which H^+ irradiation was not performed with O^{2+} irradiation. Moreover, in the case that H^+ irradiation was performed sequentially after O^{2+} irradiation, the increase of the peak area is more degraded than in the case that H^+ irradiation was performed simultaneously with or prior to O^{2+} irradiation.

In comparison to the same fluence irradiation with each ion beam by using TRIM code, the average dpa in the measurable depth with FT-IR PAS in the sample irradiated with the single O^{2+} ion beam is estimated to be about 10 and 100 times larger than that in the sample irradiated with the single He^+ and the single H^+ ion beam, respectively. Therefore, it is believed that the formation of defects in the samples irradiated with the triple ion beams is mainly attributed to the effect of the O^{2+} irradiation.

Therefore, this result may suggest that H^+ implantation affects the generation of hydroxyl near the surface by trapping hydrogen, and the effect of implantation is larger in the case where the implantation is performed after introducing the defects than that performed simultaneously. However, the number of data is not enough, especially for the single irradiation of O^{2+} in different dpa, to examine the effect of H^+ implantation sufficiently. Further examination is required to verify the effect both qualitatively and quantitatively.

In addition, it must be noted that the hydrogen-trapping sites as observed in this study would also trap tritium generated in the fusion environment and would disturb the rapid recovery of tritium from the breeding material. And the formation of TiO_2 may suggest the formation of Li_2O according to the reaction $Li_2TiO_3 \rightarrow TiO_2 + Li_2O$. If the increase in the amount of hydroxyl near the surface observed in this study would mean the possibility of LiOH formation, it may affect the compatibility of Li_2TiO_3 with other materials, i.e., stainless steel as structural materials. Unfortunately, there are few studies about tritium release behavior from and compatibility of breeding materials with other materials, such as stainless steel, in fusion reactor blanket under heavy irradiation environment. Further study is required to verify such issues under heavy irradiation environment by using ion beam irradiation, fast reactor irradiation, and so on.

4. Conclusions

The microstructural changes in Li_2TiO_3 irradiated with the H^+, He^+ and O^{2+} beams were observed by FT-IR PAS. The results suggest that the amount of TiO_2 formed is proportional to the dpa and that the method of irradiation, that is, single, simultaneous triple or sequential triple irradiation, does not affect the dependence of formation of TiO_2.

On the other hand, defects and/or radiolytic products generated by irradiation is considered to form trapping sites for hydrogen near the surface. It is found that the amount of such defects and/or radiolytic products is found to be strongly affected not only by the dpa, but also by the method of irradiation. It is suggested that simultaneous and sequential H^+ implantation with generating the defects and/or radiolytic products degrades the generation of hydroxyl near the surface by hydrogen trapping with the irradiation defects and/or radiolytic products. The effect of implantation is seemed to be larger in the case where the implantation is performed after introducing the defects than that performed simultaneously.

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