ION-IMPLANTED DEUTERIUM RELEASE BEHAVIOR FROM Li-BASED ADVANCED CERAMICS

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The behavior of ion-implanted deuterium in advanced lithium orthosilicate (Li_4SiO_4) pellets with addition of lithium metatitanate (Li_2TiO_3), and in reference Li_4SiO_4 pellets, has been studied. Thermal desorption spectroscopy (TDS) was used to examine the deuterium interaction with radiation defects in materials. Deuterium gas release from studied ceramics has revealed a clear dependence of deuterium trapping behavior on phase composition. The trap strength of radiation defects formed in lithium titanate was found to be higher than in lithium orthosilicate.

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INTRODUCTION

During the past decades, fusion reactor fuels such as deuterium and tritium have been extensively investigated due to increasing interest in nuclear fusion energy. Tritium, which is rare in nature, needs to be fabricated by tritium breeder materials. It has been proposed by the nuclear community to generate tritium by neutron irradiation of lithium-containing materials. These materials include liquid tritium breeder and solid tritium breeder materials. Due to problems with the use of liquid breeder materials (magnetohydrodynamic effects reduce liquid Li mobility; lithium-induced corrosion of facing structural materials; losses of lithium due to its volatility) there was a demand for solid ceramic materials breeder.

Among the commonly investigated tritium breeder materials, lithium orthosilicate (Li_4SiO_4) and lithium titanate (Li_2TiO_3) are recognized as some of the most promising solid tritium breeder materials because of its considerable lithium atomic density, low activation, excellent chemical stability, and low-temperature tritium release performance [1, 2]. In addition, Li_4SiO_4 and Li_2TiO_3 are regarded as the most favorable ceramics due to their satisfactory thermo-mechanical properties [3].

In recent years, the biphasic Li_2TiO_3-Li_4SiO_4 breeding material has been fabricated to combine the advantages of Li_4SiO_4 and Li_2TiO_3 [4-6]. This biphasic ceramic material offers promising opportunities for achieving balanced tritium release characteristics and improved mechanical properties [7].

The ability of breeder materials to release tritium is one of their most critical characteristics. Tritium release and generation rates must be balanced during fusion reactor operation because low tritium release rates result in high tritium retention, which is unacceptable from an economic and safety standpoint.

Despite extensive research in the field of tritium release behavior in Li-based ceramic materials, a comprehensive model of tritium release kinetics has still not been determined. Therefore, it is necessary to investigate the tritium migration process and understand the release mechanism of tritium in ceramic breeding materials.

Li-based ceramic materials are exposed to fusion neutrons in the fusion reactor blanket, where nuclear reactions of $^6Li(n,\alpha)T$ or $^7Li(n,n\alpha)T$ lead to the production of tritium. According to estimates that account for nuclear heating, the temperature distribution of the solid breeding material in Test Blanket Modules (TBM) ranges between 573 and 1173 K [8]. It is expected, that a small amount of tritium can remain in the low temperature region of the blanket during ITER operation, despite the fact that it is preferable for the tritium to be recovered completely throughout the entire region [9]. Consequently, the retention and desorption behavior of tritium in advance ceramics should be examined in order to assess the tritium inventory in Li-based ceramic materials in the TBM of ITER and the blanket of the demonstration reactors.

Due to the deficiency of 14 MeV neutron sources and the lower content of tritium in nature, the release behavior of ion implanted deuterium in ceramic breeding materials has been used to simulate the radiation effects of high-energy neutrons [1, 10, 11].

The damage caused by a D^+ ion beam is not entirely comparable to that caused by a neutron exposure. However, the irradiation effects caused by deuterium implantation greatly reduce the difficulty and cost of analysis, providing more experimental data for the tritium migration process in ceramic materials. The use of deuterium to simulate neutron irradiation is expected to provide useful data for investigating the behavior of tritium in ceramic breeding materials, including tritium diffusivity, its retention and desorption characteristics.

The behavior of deuterium interaction with Li_4SiO_4 ceramics with and without Li_2TiO_3 addition was recently studied by means of ion irradiation combined with thermal desorption spectroscopy [12]. It was shown that ion-implanted deuterium is rather easily desorbed in the temperature range of 290...650 K. At the same time, deuterium gas release showed some uncertainty in the dependence of deuterium trapping behavior on phase composition.

The goal of this paper is to investigate the influence of different composition of ceramics on the release behavior of implanted deuterium ions.

1. MATERIAL AND METHODS

The advanced Li_4SiO_4 pellets with Li_2TiO_3 as a secondary phase were investigated together with the reference Li_4SiO_4 pellets. The reference Li_4SiO_4 pellets (0 mol.% Li_2TiO_3) consisted of two crystalline phases, Li_4SiO_4 as the primary phase and Li_2SiO_3 as a secondary phase due to 2.5 wt% excess of SiO_2 (Table).

Phase composition of the advanced ceramic

Sample №	Phase composition, mol. %
1	90 % Li_4SiO_4 + 10 % Li_2SiO_3
2	80 % Li_4SiO_4 + 20 % Li_2TiO_3
3	70% Li_4SiO_4 + 30 % Li_2TiO_3

It should be noted that lithium ceramics will be used in the form of pebbles in the blanket. The pellets instead of pebbles were used in the current study in order to eliminate the effect of surface curvature, thereby providing normal ion beam incidence to the entire target surface.

The pellets were irradiated with a 25 keV D_2^+ (12.5 keV/D^+) ion beam with an ion flux of 4.0×10^{17} D^+ $m^{-2}s^{-1}$ up to an ion fluence of 1.0×10^{21} $D^+ m^{-2}$. The calculated distribution profiles of the radiation damages and the implanted deuterium ions in the irradiated pellets were simulated using SRIM code [13] (Fig. 1).
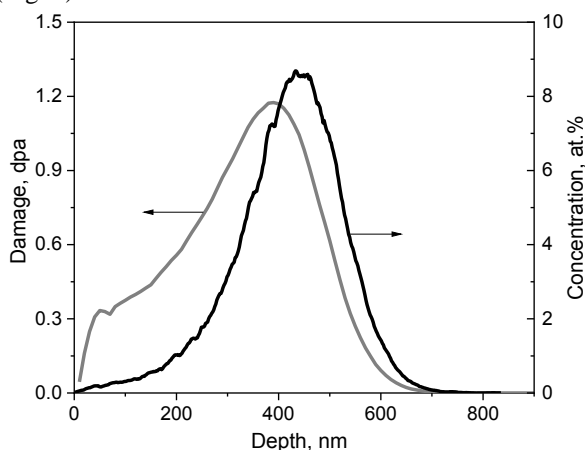

Fig. 1. Depth distribution profiles of damage and concentration for 25 keV deuterium ions in Li_4SiO_4 ceramic calculated by SRIM for a dose of $1 \cdot 10^{17}$ D^+/cm^2

The implanted deuterium release behavior was examined by the thermal desorption spectroscopy. TDS experiments were conducted with the same procedures for each sample. The sample was preheated at 1200 K for 15 min to remove impurities such as hydroxides and hydrocarbons. After preheating treatment, deuterium ions were implanted into the sample at 290 K. In situ TDS measurements were performed just after D_2 implantation in the irradiation chamber. The residual gas pressure in the experimental chamber was measured to be ~$5 \cdot 10^{-5}$ Pa.

The sample holder made of Ta plate was used to fix pellets, and the sample was heated by indirect resistive heating during the annealing. The sample temperature was increased at a heating rate of 1 Ks^{-1}, and desorbed D_2 molecules were measured by a monopole mass spectrometer. The temperature range was room temperature to 1200 K in all TDS experiments.

2. RESULTS AND DISCUSSION

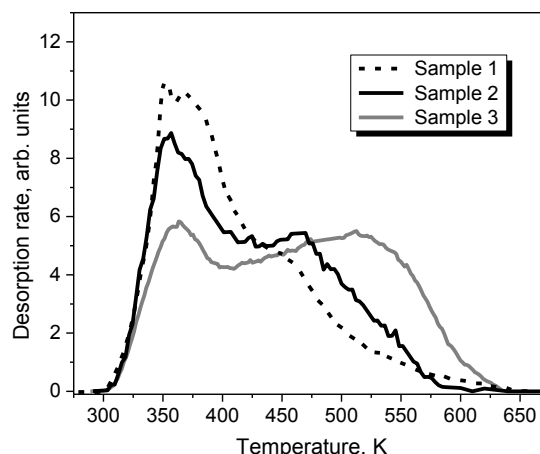The deuterium release rate as a function of temperature is shown in Fig. 2 for the three studied materials.

Fig. 2. Deuterium TDS spectra from advanced ceramics irradiated with deuterium ions to a dose of $1 \cdot 10^{21}$ D/m^2 at room temperature

In the current study, almost all the deuterium was released as D_2 molecules. Deuterium evolution was observed in the temperature range of 300...650 K, and each release spectrum appears to composed of two visually distinguishable D_2 desorption peaks. The low-temperature stage is characterized by the same desorption peak temperature located at around 365 K for all studied samples. The location of high-temperature stage varies from 430 to 520 K depending on phase composition of the sample.

A similar deuterium release behavior in the temperature range 300...650 K was observed in the TDS spectra of deuterium from Li-based ceramics [10, 11] as a low-temperature desorption stage in the structure of a more complex spectrum obtained after an order of magnitude higher irradiation dose.

Our previous study [12] has demonstrated that the desorption of implanted deuterium in Li-based ceramics is limited predominantly by intragranular diffusion of deuterium and its trapping by radiation defects. The relatively low temperature of deuterium desorption (365 K) indicates its high diffusion mobility.

High diffusivity of implanted deuterium in different grades of Li-based ceramics was also shown at examining deuterium atoms redistribution by means of nuclear reaction analysis [14]. Significant discrepancies between the measured and the simulated by SRIM depth profiles were observed after 100 keV deuterium implantation in ceramics. These discrepancies were attributed to deuterium diffusion, which occurred even at near room temperature. In the as-implanted conditions, the deuterium concentration was higher at the surface than in the bulk, indicating that the deuterium release is

greatly influenced by the ceramics surface. Annealing at temperatures up to 373 K promoted deuterium release from all samples examined. For annealing temperatures above 423 K, the deuterium concentration was negligible for all samples, indicating that deuterium is completely outgassed.

It is important to note, that the lower heating rate of $1~Ks^{-1}$ used in the present case, instead of $6~Ks^{-1}$ in our previous study [12], caused a displacement in the onset temperature of gas evolution and the maxima of desorption peaks towards lower temperatures and, simultaneously, contributed to the obtaining of a well-resolved TDS peaks in temperature.

Fig. 3 shows the results of peak separation analyses with the Gaussian distribution function performed for Sample 1 and Sample 3. Two D_2 release peaks (365 and 430 K) demonstrate the best fit for the release spectrum of Sample 1, while three peaks (360, 430, and 530 K) were needed to fit the release spectrum of Sample 3.
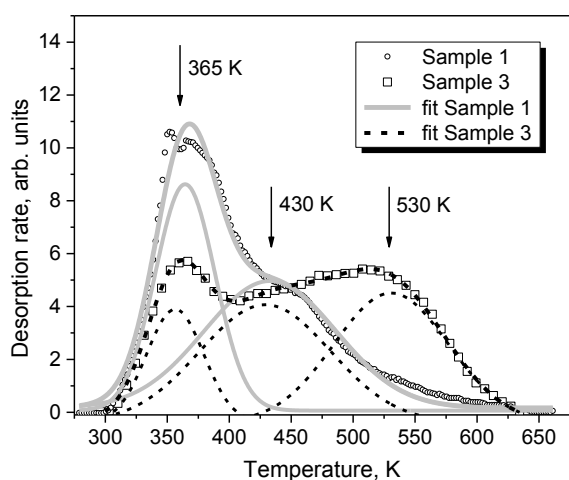

Fig. 3. Peak separation analyses using the Gaussian distribution function for Samples 1 and 3

Almost identical location of low-temperature peak (~365 K) for all investigated ceramics implies that diffusion process does not depend remarkably on ceramic phase composition. The desorption peak with a maximum at 430 K appears to be associated with deuterium de-trapping from defects formed by radiation damage in lithium orthosilicate. The high-temperature peak at 530 K is observed only in samples with Li_2TiO_3 additions (peak separation not shown for Sample 2) and, apparently, could be attributed to deuterium de-trapping from radiation defects in lithium titanate. Traps formed in Li_2TiO_3 contribute to an increase in the overall amount of trapped deuterium, that leads to a decrease in amount of freely diffusing deuterium and, consequently, to a decrease in the amplitude of the low-temperature peak. The higher desorption temperature of deuterium from traps associated with Li_2TiO_3 testifies the stronger trap strength of defects in lithium titanate compared to defects in lithium orthosilicate.

It is noteworthy, that the release of tritium after neutron exposure occurs at higher temperatures [1], compared to release temperature range of ion-implanted deuterium. This could be related to the following effects. Due to the ability of thermal neutrons to easily penetrate crystalline grains within a several micrometers, tritium can be uniformly generated in these grains under neutron exposure. In contrast, keV-energy deuterium implantation led to its distribution in the projective range of about a few hundreds of nanometers. Such a difference produces hydrogen isotopes with different diffusion lengths to the desorption surface. It is expected that because of the shorter diffusion length under deuterium irradiation, the gas release stage associated with implanted deuterium diffusion would occur at lower annealing temperatures, whereas the long diffusion length in the case of neutron exposure would delay tritium release. In addition, tritium release from the ceramic bulk in the case of neutron irradiation can be affected by a number of factors, such as interaction (adsorption/desorption) with grains surface, pores, etc. These effects might retard tritium transport in neutron-exposed ceramics resulting in tritium release at higher temperatures. Furthermore, neutron irradiation experiments are usually performed at temperatures several tens of degrees above room temperature, hence low-temperature desorption stages may not be present in the TDS spectrum due to gas release during irradiation.

Thus, the diffusion of tritium in neutron-exposed ceramics is a fairly complex process, which is numerically characterized by the effective diffusion coefficient, in which the activation energy of diffusion (0.63...1.5) eV [15, 16]) appears to be a superposition of activation energies of several involved processes. In contrast, the in tragranular diffusion of ion-implanted deuterium represents the interstitial migration of deuterium atoms through ceramic lattice, which is characterized by a significantly smaller value of diffusion activation energy (0.33...0.52) eV [17, 18]).

Recent studies have suggested that reactions on the grain surface are also very important for understanding tritium release behavior. Reported data indicate that if water or any hydrogen-containing purge gas was involved in the reaction, tritium was mainly released in the form of HT, HTO+HT, and H_2O, while in the vacuum environment, tritium predominantly desorbed as HT and T_2 [1]. Hence, the vacuum environment avoids the uncontrolled surface effects, and helps to reveal the deuterium/tritium release mechanism.

There is also an assumption that the low-temperature stages of desorption (particularly, at near 360 K) can be associated with the physical or chemical adsorption of deuterium on the ceramic surface [11]. However, it is unlikely that at room temperature and vacuum of the order of $(1...2) \cdot 10^{-4}$ Pa maintained during irradiation, significant amount of deuterium can be adsorbed at the surface in our experiments. Nevertheless, further studies are needed to resolve this issue using complex of experimental techniques allowing to analyze hydrogen isotopes redistribution within the material, the kinetics of its release, and the surface conditions.

CONCLUSIONS

To evaluate the tritium inventory and recover the tritium produced in the tritium breeder, the tritium has to be desorbed completely under the temperature

distribution. In order to simulate this behavior, the advanced Li$_4$SiO$_4$ pellets with Li$_2$TiO$_3$ as a secondary phase and the reference Li$_4$SiO$_4$ pellets were irradiated with deuterium ions (12.5 keV D$^+$) up to an ion fluence of $1.0 \cdot 10^{21}$ D/m^2. After the irradiation, the desorption behavior of retained deuterium in ceramics of different composition was examined using a thermal desorption spectroscopy. The main results are summarized as follows.

Deuterium release in all studied ceramics occurs in the temperature range of 300...650 K, but represented by a different number of desorption stages.

The low-temperature stage associated with deuterium diffusion process is characterized by the same desorption peak temperature (365 K) for all examined materials, that indicates the independence of deuterium diffusivity on phase composition of ceramics.

The high-temperature desorption stages are related to the deuterium de-trapping from radiation-induced traps. The intensity of peaks depends on the ratio of Li$_4$SiO$_4$ and Li$_2$TiO$_3$ in the composition of ceramic. The trap strength of defects formed in lithium titanate is higher than in lithium orthosilicate.

ACKNOWLEDGEMENTS

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ГАЗОВИДІЛЕННЯ ІОННО-ІМПЛАНТОВАНОГО ДЕЙТЕРІЮ З УДОСКОНАЛЕНОЇ КЕРАМІКИ НА ОСНОВІ Li

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Досліджено поведінку іонно-імплантованого дейтерію в удосконалених таблетках ортосилікату літію (Li$_4$SiO$_4$) з додаванням метатитанату літію (Li$_2$TiO$_3$) та в еталонних таблетках Li$_4$SiO$_4$. Для вивчення взаємодії дейтерію з радіаційними дефектами в матеріалах використовувалася термодесорбційна спектроскопія (ТДС). Виділення дейтерію з досліджуваних керамік виявило чітку залежність характеру захоплення дейтерію від фазового складу. Було встановлено, що енергія зв'язку дейтерію з радіаційними дефектами в титанаті літію вища, ніж у ортосилікаті літію.