Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 329–333 (2004) 880–884
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Thermal desorption of deuterium from ion irradiated $Be_{12}Ti$

H. Iwakiri [a,*], K. Yasunaga [a], N. Yoshida [a], M. Uchida [b], H. Kawamura [b]

[a] Research Institute for Applied Mechanics, Kyushu University 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan
[b] Oarai Research Establishment, Japan Atomic Energy Research Institute, Oarai, Higashi-Ibaraki, Ibaraki 311-1394, Japan

Abstract

Thermal desorption of deuterium from $Be_{12}Ti$ irradiated by D_2^+ ions and microstructural change during irradiation were examined to understand deuterium retention and desorption properties. Total retention of deuterium in $Be_{12}Ti$ is much smaller than that of beryllium over a wide temperature range. For implantation of 1×10^{21} D_2^+/m^2 at room temperature, 10% of implanted deuterium is retained and most of this is desorbed near 400 K, where a high-density of cavities were formed. In the case of beryllium, 83% of implanted deuterium is retained. These results indicate that deuterium trapping efficiency of cavity in the $Be_{12}Ti$ is much lower than that in beryllium.

1. Introduction

For the neutron multiplier, beryllium (Be) metal is the reference material for blanket design. However, it may not be acceptable for to the DEMO blanket, which requires high temperature and high neutron dose, because of high reactivity and large swelling. Therefore, it is necessary to develop an advanced material for a neutron multiplier that has high temperature resistance and high radiation resistance. Berylides such as $Be_{12}Ti$ and $Be_{12}V$ have been suggested as promising candidates for advanced neutron multipliers because they have high melting point, high beryllium content, fast decay of gamma dose rate, and good chemical stability, etc. [1].

The behaviour of hydrogen isotopes in the neutron multiplier will influence the safety of the reactor. In this study thermal desorption experiments and microstructure observation of deuterium irradiated $Be_{12}Ti$ were performed to expand the understanding of fundamental aspects of hydrogen behavior in $Be_{12}Ti$.

2. Experimental procedures

$Be_{12}Ti$ specimens used in the present work were fabricated by the hot isostatic pressing (HIP) process by NGK Insulators, Ltd. [2]. Irradiation with 8 keV-D_2^+ ions were carried out in an ultra-high vacuum evacuation apparatus equipped with a small duo-plasmatron type ion gun [3]. After irradiation, the specimens were transferred into the TDS apparatus, where the thermally desorbed deuterium gas was measured with a quadruple mass spectrometer. Deuterium desorption rate was calculated from D_2 and HD molecules. The temperature of the specimens was increased up to 1000 K with a ramp rate of 1 K/s.

Pre-thinned samples for transmission electron microscope observation were obtained by twin-jet electro-polishing. The in situ observation under D_2^+ ion irradiation was conducted using a 200 kV transmission electron microscope equipped with a low energy ion accelerator. Details of the facility were described elsewhere [3].

3. Results

3.1. Retention and thermal desorption of deuterium

Fig. 1 shows thermal desorption spectra of D from $Be_{12}Ti$ irradiated with 8 keV-D_2^+ ions up to 6×10^{21}

* Corresponding author. Tel.: +81-92 583 7719; fax: +81-92 583 7690.
E-mail address: iwakiri@riam.kyushu-u.ac.jp (H. Iwakiri).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.280

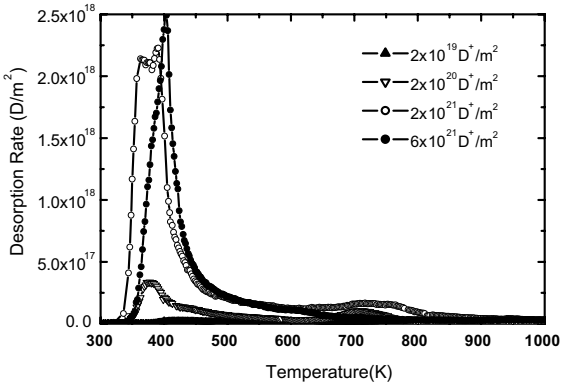

Fig. 1. Thermal desorption spectra of D from $Be_{12}Ti$ irradiated with 8 keV-D_2^+ ions up to 6×10^{21} D^+/m^2 at room temperature.

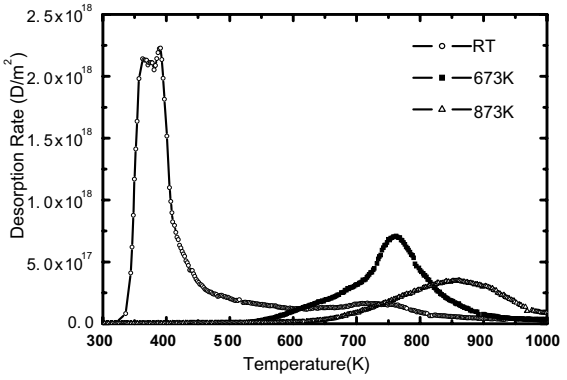

Fig. 3. Thermal desorption spectra of D from the $Be_{12}Ti$ irradiated with 8 keV-D_2^+ at several temperatures up to 873 K.

D^+/m^2 at room temperature. The desorption can be classified into two groups; a sharp stage on the low temperature side (350–450 K) and a broad stage on the high temperature side (450–800 K). The desorption stages are named here the low temperature and high temperature stage. Both desorption stages increase with increasing fluence up to 2.0×10^{21} D^+/m^2.

Total amounts of desorbed D from $Be_{12}Ti$ and Be irradiated with 8 keV-D_2^+ at room temperature are plotted in Fig. 2 as a function of ion fluence. The straight dashed line in the figure shows 100% retention. It is clear that the trapping efficiency of deuterium in the $Be_{12}Ti$ is much lower than that in Be.

Fig. 3 shows thermal desorption spectra of deuterium from the $Be_{12}Ti$ irradiated with 8 keV-D_2^+ at several temperatures up to 873 K. The total amount of desorption decreases with increasing temperature. In the case of deuterium irradiation at 673 K, the desorption at the low temperature stage is diminished, but the desorption at the high temperature stage increases and majority of the trapped deuterium is desorbed between 600 and 900 K. With increasing irradiation temperature, the high temperature stage shifts toward higher temperatures.

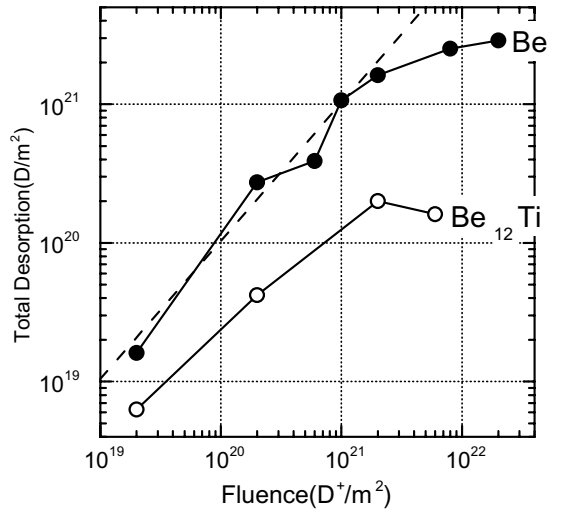

Fig. 2. Total amount of desorbed D from the $Be_{12}Ti$ and Be irradiated with 8 keV-D_2^+ at room temperature.

3.2. Microstructure evolution under deuterium ion irradiation

Fig. 4 shows microstructural evolution in $Be_{12}Ti$ at room temperature under irradiation with 8 keV-D_2^+ ions. No clear defects were observed by TEM at low fluence less than 2×10^{20} D^+/m^2. A high density of fine cavities, probably bubbles of deuterium, of 2–3 nm in size were observed at 6×10^{20} D^+/m^2. With increasing dose, the cavities grow gradually at first and grow further by coalescing. Interstitial-type defects, e.g., interstitial loops, were seldom observed at any fluence. This means that the nucleation of interstitial loops is difficult in $Be_{12}Ti$.

Transmission-electron micrographs of Be irradiated at room temperature by D_2 ions at 8 keV with doses of (a) 8.6×10^{20} D^+/m^2, (b) 4.0×10^{21} D^+/m^2, (c) 2.0×10^{22} D^+/m^2 are shown in Fig. 5 for comparison with Fig. 4. The cavity size in Be does not grow more than a few nm even at very high fluence, while that in $Be_{12}Ti$ grows large as shown in Fig. 4.

Fig. 6 shows changes in microstructures in $Be_{12}Ti$ formed by the irradiation at room temperature to a dose of 2×10^{21} D^+/m^2, followed by isochronal annealing (100 K step, 30 min). No significant changes occurred up to 473 K, while the cavities start to migrate and coalesce between 473 and 573 K. Migration and coalescence of the cavities continue up to 1173 K. It was observed in situ that relatively small cavities suddenly disappeared, probably when they reached the surface and lost the

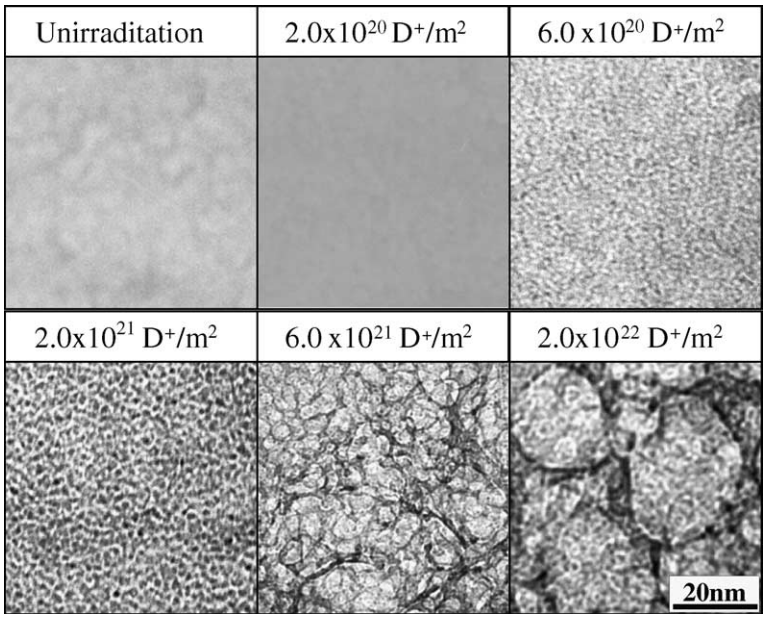

Fig. 4. Microstructural evolution of $Be_{12}Ti$ at room temperature under irradiation with 8 keV-D_2^+ ions.

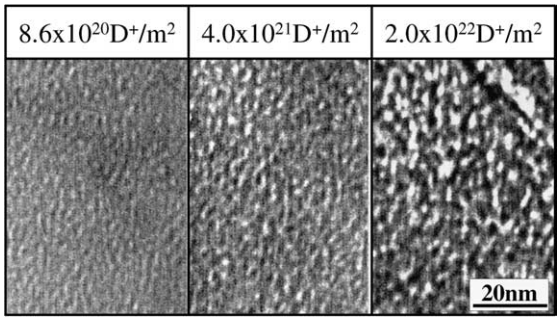

Fig. 5. Microstructural evolution of Be at room temperature under irradiation with 8 keV-D_2^+.

trapped deuterium and then shrank quickly by surface diffusion and emission of thermal vacancies. All of the cavities finally disappeared at 1273 K.

4. Discussion

Fig. 7 shows thermal desorption spectra of D released from $Be_{12}Ti$ and Be [6] irradiated to 2×10^{21} D^+/m^2 at room temperature and 673 K. In the case of $Be_{12}Ti$, 10% of implanted deuterium is retained and most of this is desorbed around 400 K. For implantation at 673 K, retention becomes smaller, about 5% for 2×10^{21} D^+/m^2, and the majority of deuterium is desorbed between 600 and 900 K. In the case of Be, however, deuterium retention is much larger than that of $Be_{12}Ti$; 83% of implanted deuterium is retained at room temperature and 66% at 673 K. Some authors also showed that two large desorption stages were formed in Be under deuterium ion irradiation [4–7] and they suggest the higher temperature side is related to cavities filled with D_2 molecules. By using SIMS and RGA (residual gas analysis), the existence of D_2 molecules in irradiated Be was confirmed by Alimov et al. [8]. As well as Be, a high density of fine cavities were formed in $Be_{12}Ti$. By migration and coalescing, as it was shown in Fig. 6, cavities disappear gradually from the surface on annealing up to 473–1273 K. Such phenomenon may be related to the broad desorption stage at high temperature, however, the partial amount of desorbed deuterium from the high temperature stage in $Be_{12}Ti$ is about 1/15 in comparison to the amount desorbed in Be. These results indicate that deuterium trapping efficiency of cavities in the $Be_{12}Ti$ is much lower than that in Be. In other words, though highly pressurized D_2 cavities can be formed in the Be, the pressure in the cavities in the $Be_{12}Ti$ is low.

On the other hand, there is no significant evidence to reveal understanding the mechanism of the low temperature stage in the $Be_{12}Ti$. In the case of Be, some hypotheses have been proposed. Wilson et al. [9] interpreted this stage as corresponding to the detrapping from amorphous beryllium hydride which decomposed at 400 K. Another interpretation was suggested by Zakharov et al. [7], that deuterium atoms are trapped at the chemisorption sites on the walls of the deuterium gas cavities. However, these hypotheses can not give reasonable explanation for the present $Be_{12}Ti$ results, since the amount of desorbed deuterium from the low

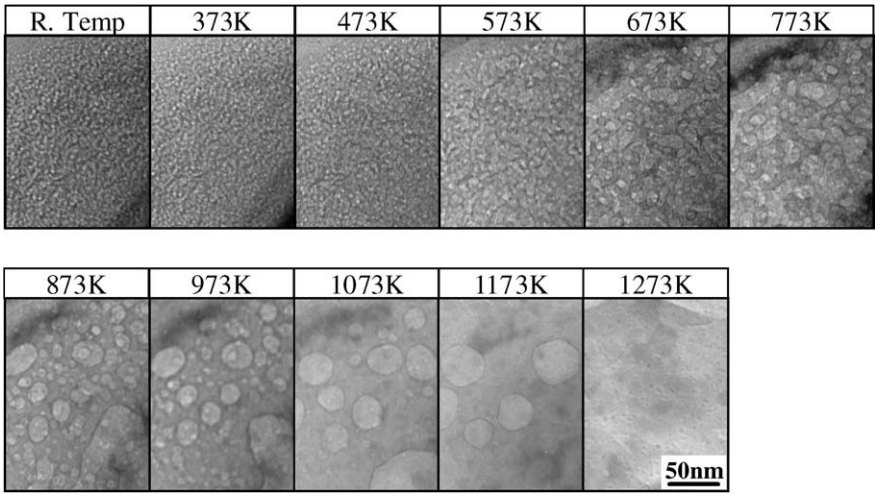

Fig. 6. Isochronal annealing (100 K-step, 30 min) of microstructure in $Be_{12}Ti$ formed by room temperature irradiation to a dose of 2×10^{21} D+/m^2.

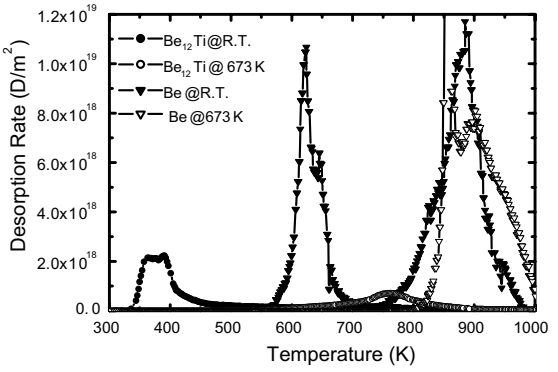

Fig. 7. Thermal desorption spectra of D released from $Be_{12}Ti$ and Be irradiated to 2×10^{21} D+/m^2 at room temperature and 673 K.

temperature stage in $Be_{12}Ti$ is much smaller than that in Be. We need more experiments to understand the details of the low temperature stage in $Be_{12}Ti$.

5. Conclusion

Thermal desorption of deuterium from 8 keV D_2^+ ions irradiated $Be_{12}Ti$ and microstructural change during irradiation and annealing were examined to understand deuterium retention and desorption of the implanted deuterium, and to identify responsible traps. The results are summarized as follows.

(1) The deuterium desorption stage of $Be_{12}Ti$ can be classified into low temperature side and high temperature side for room temperature deuterium irradiation. In the case of deuterium irradiation at 673 K, the desorption at the low temperature stage is diminished, but the desorption at the high temperature stage increases.
(2) Total retention of deuterium in $Be_{12}Ti$ is much smaller than that in Be over the wide temperature range.
(3) In $Be_{12}Ti$ as well as in the Be, a high density fine cavities were formed. With increasing dose, however, the cavity size in $Be_{12}Ti$ grows gradually at first and grows further by coalescing, unlike Be.
(4) Possible deuterium trapping sites for the high temperature stage are cavities, as is the case with Be. However, the deuterium trapping efficiency of cavities in the $Be_{12}Ti$ is much lower than that in Be.

Acknowledgements

We are grateful to Dr T. Shibayama for helpful suggestions and observations.

References

[1] M. Uchida, E. Ishitsuka, H. Kawamura, Fus. Eng. Des. 69 (2003) 499.
[2] H. Kawamura, M. Uchida, V. Shestakov, J. Nucl. Mater. 307–311 (2002) 638.
[3] T. Muroga, R. Sakamoto, M. Fukai, N. Yoshida, T. Tukamoto, J. Nucl. Mater. 196–198 (1992) 1013.
[4] W.R. Wampler, J. Nucl. Mater. 122&123 (1984) 1598.
[5] R.A. Langley, J. Nucl. Mater. 122&123 (1979) 1123.

[6] N. Yoshida, S. Mizusawa, R. Sakamoto, T. Muroga, Fus. Technol. 30 (1996) 798.
[7] A.P. Zakharov, A.E. Gorodetsky, V.Kh. Alimov, S.L. Kanashenko, A.V. Markin, J. Nucl. Mater. 241–243 (1997) 52.
[8] V.kh. Alimov, V.N. Chernikov, A.P. Zakharov, J. Nucl. Mater. 241–243 (1997) 1047.
[9] K.L. Wilson, R.A. Causey, W.L. Hsu, B.E. Mills, M.F. Smith, J.B. Whitley, J. Vac. Sci. Technol. A 8 (1990) 1750.