Effect of heat treatment of titanium beryllide on tritium/hydrogen release

Vladimir Chakin[a,*], Rolf Rolli[a], Ramil Gaisin[a], Petr Kurinskiy[b], Jae-Hwan Kim[b],
Masaru Nakamichi[b]

[a] *Karlsruhe Institute of Technology, Institute for Applied Materials, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[b] *Fusion Energy Research & Development Directorate, Rokkasho Fusion Institute, Department of Blanket Systems Research, Breeding Functional Materials Development Group, National Institutes for Quantum and Radiological Science and Technology, QST, Japan*

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ABSTRACT

In the present paper, a homogenization heat treatment at 1473 K for 8 h was carried out with the aim to obtain the single-phase Be12Ti structure in the pebbles of three Be-Ti compositions: Be-7.0Ti, Be-7.3Ti, Be-7.7Ti at.%. After the heat treatment the average porosity in the pebbles increased from 5 to 8% to 36–47%, which resulted in lower amount of tritium/hydrogen retention during the loading. Temperature-programmed desorption tests showed that the performed heat treatment facilitates tritium/hydrogen release from Be-Ti pebbles. Assessment of the effective activation energies of tritium desorption reveals that the tritium release from titanium beryllide occurs much more easier than from pure beryllium.

1. Introduction

Due to lower swelling under irradiation and higher resistance to oxidation, new titanium beryllide compounds are considered to replace beryllium as neutron multiplier material in Japanese and European DEMO breeding blanket designs [1–4]. During neutron irradiation of beryllium in fusion reactors significant amounts of helium and beta-radioactive tritium are produced. Lower retention and higher release of tritium from Be-containing material is essential for the blanket to facilitate its handling and recycling after end-of-life. However, tritium release and retention behavior of titanium beryllides were not sufficiently studied to date. Since neutron irradiation with high fluxes to produce helium and tritium is a very expensive procedure, the saturation of beryllium materials can be performed by using the high-temperature loading in the tritium/hydrogen gas mixture [5]. This method allows for the assessment and pre-ranking of the materials based on their tritium release and retention behavior after thermal-programmed desorption (TPD) tests without irradiation. In this paper, effects of heat treatment and Ti content in Be-Ti compounds on tritium release and retention are studied.

2. Experimental

The titanium beryllide pebbles having a diameter of 1 mm (Fig. 1) were produced by the rotating electrode method (REM) (KREP-1500, Kaken Co., Ltd., Japan). The plasma-sintering method (PSM) (KE-PasIII,

Kaken Co., Japan) was used to synthesize electrodes from beryllium-titanium powder mixture with appropriate beryllium and titanium contents [2,6]. In this paper Be-7Ti, Be-7.3Ti, and Be-7.7Ti (at.%) intermetallic compounds were chosen for the study. According to the Be-Ti phase diagram (Fig. 2), these compositions should be formed by a $Be_{12}Ti$ intermetallic phase and may contain α-Be.

A homogenization heat treatment was performed for the Be-Ti pebbles. It was carried out at 1473 K for 8 h to ensure maximal amount of $Be_{12}Ti$ phase [7–9]. For simplicity, the as-received and homogenized states of Be-Ti pebbles are indicated as AR and HT, respectively.

The tritium/hydrogen loading of the Be-Ti pebbles was performed in the $^1H_2$ + 500 appm $^3H_2$ gas mixture at 1123 K for 6 h at 4 bar. During the temperature-programmed desorption (TPD) tests, the specimens were heated with ramping rates of 1 or 7 K/min up to 1373 K and annealed for 3 h. The gas mixture of high-purity helium with small addition of hydrogen (^4He + 0.1 vol.% $^1H_2$) was used as a purge gas to transport the released species from a furnace with the pebbles to a proportional counter (PC). A Zn-bed was placed between the furnace and the PC. It was heated to 663 K, a temperature that allows the transformation of tritium water to tritium gas to avoid tritium water absorption in the pipes and in the PC. For the same reason, the gas pipes in the manifold are heated to 573 K during the TPD tests. Thus, the released tritium reaches the PC mainly in the form of $^1H^3H$ [10].

Microstructural examinations were carried out using optical microscopy in normal and polarized light on ground and mechanically polished samples. ImageJ software was used to measure dimensions of
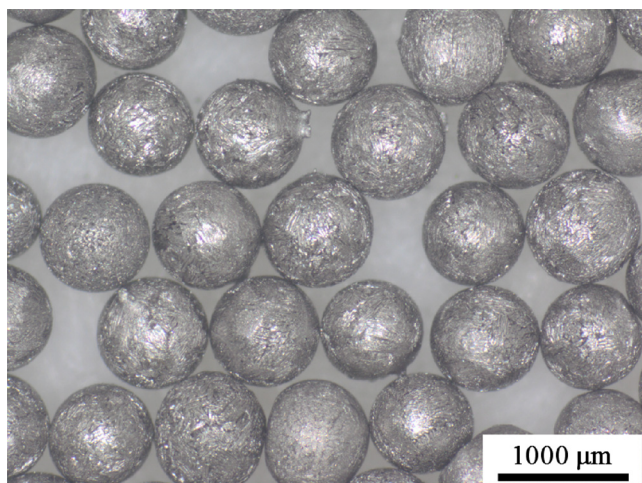
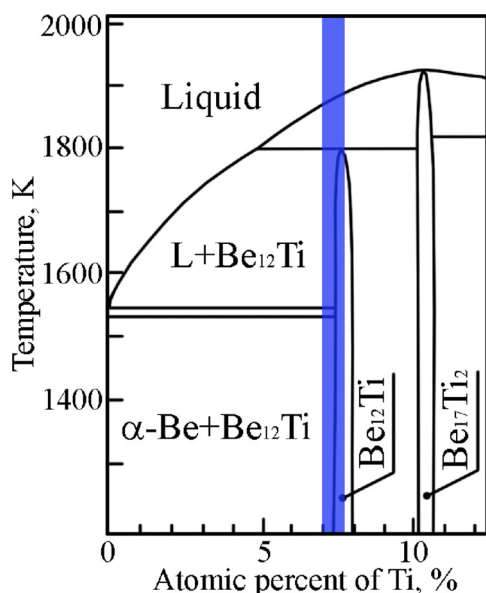**Fig. 1.** Optical micrograph of the Be-Ti pebbles produced by REM.

Fig. 2. An abridged Be-Ti phase diagram. Compositions under study are shaded with a blue color (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

microstructure features. Porosity level was calculated by the systematic point count method on 5–6 cross-sections of Be-Ti pebbles for each state.

3. Results and discussion

3.1. Microstructure

Figs. 3–5a represent cross-sections of as-received Be-Ti pebbles manufactured by the REM. Optical microscopy on polarized light (right parts of images) showed that the pebbles have a coarse grain microstructure with needle-shaped crystallites, having lengths up to 200 μm and a mean thickness of about 15 μm. On the left part of images obtained in normal light one can see considerable amount of pores. With Ti content increase, the average porosity changes from 5 to 8% (Fig. 6a). The pores are mainly situated between needles and reach about 50 μm in length.

The observed microstructure could be formed during solidification through the peritectic and eutectic reactions (Fig. 1). Firstly, during cooling, crystallites of $Be_{17}Ti_2$ intermetallic phase precipitate in the liquid. At ≈1823 K, the peritectic reaction occurs according to L + $Be_{17}Ti_2$ → $Be_{12}Ti$. Owing to the high cooling rate of pebbles, titanium atoms in $Be_{17}Ti_2$ could not quickly diffuse to form $Be_{12}Ti$ on the edge of the crystallites, and, consequently, more beryllium atoms stayed in the liquid. Due to the fact that the $Be_{12}Ti$ crystallites precipitated in the liquid phase, they reached fairly large sizes. In the next crystallization step, the remaining material, supersaturated with liquid beryllium, transformed into a mixture of β-Be and $Be_{12}Ti$ according to the eutectic reaction L → β-Be + $Be_{12}Ti$ (Fig. 1). Therefore, more Be phase formed in eutectic among coarse $Be_{12}Ti$ crystallites. The rapid cooling rate could also cause the formation of considerable internal shrinkage porosity during liquid solidification between $Be_{12}Ti$ and β-Be. According to [7–9,11,12], the pebbles can also contain a considerable amount of metastable $Be_{17}Ti_2$ phase. The following homogenization of as-cast pebbles from titanium beryllide should be performed to ensure the single phase composition which includes only $Be_{12}Ti$ phase (the compositional target).

The homogenization heat treatment resulted in the formation of highly developed porosity in all Be-Ti compositions (Figs. 3–5b). The average porosity ranges from 36 to 47% (Fig. 6a). The length of pores reaches 300 μm, the mean width of pores is 20 μm. Owing to the high porosity, other microstructural features can only be poorly identified using optical microscopy.

The rapid cooling of the pebbles made by REM led to formation of a non-equilibrium structure with higher amount of beryllium phase between $Be_{12}Ti$ crystallites and metastable $Be_{17}Ti_2$ phase. The optimization of the heat treatment parameters was performed in [7–9]. The authors showed that homogenization at 1673 K for 1 h or 1473 K for 8 h are optimal to eliminate Be and $Be_{17}Ti_2$ phases keeping only $Be_{12}Ti$. The dimension changes of the beryllide pebbles after homogenization were reported not to be caused by internal cracks or pores. This means that the nature of the numerous large pores in the homogenized $Be_{12}Ti$ pebbles is different compared to the pore formation process in beryllium pebbles after high-dose neutron irradiation where large dimensional and density changes (so-called swelling) were discovered [13].

On the other hand, the observation of the formation of such a large amount of porosity during the homogenization heat treatment can be explained by a difference in diffusion rates of Be and Ti. Due to this, the beryllium phase was dissolving faster than the $Be_{12}Ti$ phase was formed. This is accompanied by significant shrinkage of the material leading to the pore formation. It can be suggested that in the pebbles after homogenization, an open-cell porosity is formed, which usually forms reaching more than 30–40% of porosity [14]. A similar open-cell porosity in pebbles from pure beryllium after neutron irradiation was observed in earlier studies [10,15–18].

Figs. 3–5c, d, represent the microstructure of Be-Ti pebbles in AR and HT states after tritium/hydrogen loading and TPD tests. One can see the formation of well-developed interconnected pores and channels. For AR state, the hydrogen loading and the desorption tests resulted in porosity increase from 5 to 8% to 20–24% (Fig. 6b). In the case of HT state, the average porosity tends to decrease down from 36 to 47% to 26–34%. Right parts of Figs. 3–5 show, that dimensions of the needle-shaped crystallites remained nearly the same as in AR state.

The formation of the open-cell porosity in AR pebbles during tritium/hydrogen loading (1123 K, 6 h) and TPD test (heating up to 1373 K, then, 3 h annealing) can be explained by the Kirkendall effect. The observed decrease in porosity for HT state may be caused by sinking of pores into channels and forming the open-cell porosity. But strictly speaking, taking into account the measurement error, the porosity of HT states after TPD did not change.