



Reactivity and deuterium retention properties of titanium-beryllium intermetallic compounds



Jae-Hwan Kim ^{a, *}, Mitsutaka Miyamoto ^b, Yuta Hujii ^b, Masaru Nakamichi ^a

^a Breeding Functional Materials Development Group, Fusion Energy Research and Development Directorate, National Institutes for Quantum and Radiological Science and Technology, QST, Japan

^b Interdisciplinary Faculty of Science and Engineering, Department of Material Science, Shimane University, Shimane, Japan

ARTICLE INFO

Article history:

Received 27 September 2016

Received in revised form

15 November 2016

Accepted 24 November 2016

Keywords:

Intermetallics

Oxidation

Heat treatment

Scanning electron microscopy

Deuterium retention

ABSTRACT

Beryllium intermetallic compounds (beryllides), such as Be_{12}Ti and Be_{12}V , are the most promising advanced neutron multipliers in demonstration (DEMO) fusion power reactors because of higher stability, lower retention, and swelling. The advanced neutron multipliers are being developed by Japan and the EU as a framework of Broader Approach (BA) activities, targeted at broadening the research fields to not only establish fabrication methods but also for their characterization. Our group has proposed a plasma sintering method for the synthesis of beryllides. When the mixed powder was plasma-sintered at the beginning of the experiment, consolidation of the target composition was so insufficient that single-phase beryllides could not be synthesized. In order to obtain single-phase beryllides, an additional homogenization treatment of the sintered beryllides at 1473 K was necessary, resulting in increased porosity. Using the homogenized powder as the starting material, single-phase Be_{12}Ti and $\text{Be}_{17}\text{Ti}_2$ intermetallic compounds were successfully synthesized. As experimental results, the hardness of the compounds was relatively low owing to low sintering density. In addition, the oxidation behavior of the beryllides, when exposed to 15% $\text{H}_2\text{O}/\text{Ar}$ at high temperatures, were investigated and the results indicate the presence, gray colored Be oxide formed on the surface in Be_{12}Ti tested at above 1073 K and Be oxide with a small fraction of white colored Ti oxide even tested at 873 K in $\text{Be}_{17}\text{Ti}_2$ phase resulting in the bigger increase of the weight gain than Be_{12}Ti . In addition, this oxidation occurring at lower temperature can be reasoned by the assumption that the existence of BeO (=oxygen content) in Be_{12}Ti (1.95%) and $\text{Be}_{17}\text{Ti}_2$ (2.95%) may facilitate increased reactivity. Furthermore, thermal expansion of $\text{Be}_{17}\text{Ti}_2$ was found out to be bigger than that of Be_{12}Ti because $\text{Be}_{17}\text{Ti}_2$ has more complex crystal structure and higher melting temperature. In terms of deuterium desorption and retention properties, the maximum peaks are detected around 600 K in beryllides, while those in beryllium occur at 800 and 980 K. From the comparison of deuterium retention, it was obvious that $\text{Be}_{17}\text{Ti}_2$ has a lower retention than Be_{12}Ti , while Be has the highest value.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Beryllium intermetallic compounds (beryllides) have received widespread attention as refractory materials [1–3] because of their excellent oxidation resistance and strength at high temperatures. In the past decade, the beryllides have demonstrated their superior function advanced neutron multipliers [4–6] in solid breeder water coolant blankets of an experimental fusion reactor, as well as a target material for an accelerator-based boron neutron capture

therapy (BNCT) [7]. In addition, as refractory materials, Beryllides have been developed by Japan and the EU as a part of Broader Approach (BA) activities targeted at the development of advanced neutron multipliers, which morphologically require a pebble type.

A new fabrication process for the synthesis of beryllide pebbles, employing a combination of plasma sintering and a rotating electrode method (REM), was suggested based on our previous research [8–10]. The fabrication of the pebbles using the REM resulted in formation of the Be_{12}Ti and $\text{Be}_{17}\text{Ti}_2$ on the surface (whereas, Be, Be_{12}Ti , and $\text{Be}_{17}\text{Ti}_2$ phases are in the cross-section) due to peritectic reaction during the REM process. Since the phase composition on the surface of the pebble predominately

* Corresponding author.

E-mail address: kim.jaehwan@qst.go.jp (J.-H. Kim).

influences its reactivity at high temperatures, further evaluation of a single-phase Be₁₂Ti and Be₁₇Ti₂ compound is necessary to clarify the reactivity at high temperature in water vapor. Specifically, the water cooling system in the test blanket module (TBM in the Japanese blanket concept) at the international thermal experimental reactor (ITER) and demonstration (DEMO) fusion reactor, may contribute to the undesirable generation of H₂ gas in case of an unexpected reaction between either beryllium or beryllide and leaked H₂O from the coolant pipe lines in case of a certain accident such as a loss of coolant accident (LOCA). This can be also considered a critical accident if it occurs with the target material of the BNCT. Therefore, beryllium-based intermetallic compounds, such as single-phase Be₁₂Ti and Be₁₇Ti₂, would be a better alternative for a potential beryllium target because of its higher melting point and stability in the presence of H₂O. However, studies on the fabrication and stability of a single-phase Be₁₂Ti and Be₁₇Ti₂ are currently insufficient. Besides, the thermal expansion of the beryllides is closely associated with the design of blanket.

In the present study, single-phase Be₁₂Ti and Be₁₇Ti₂ were successfully fabricated through a combinatorial process involving an annealing of the powders and plasma sintering. To evaluate its stability at high temperatures, the weight gain of the single-phase Be₁₂Ti and Be₁₇Ti₂ samples were investigated at 673, 873, 1073, 1273, and 1473 K under 15% H₂O/Ar. The water was introduced at room temperature before ramping. As thermal analysis of the samples, coefficient of thermal expansion was investigated. Furthermore, D⁺ retention and release properties of irradiated samples were evaluated to verify the hydrogen isotope desorption property.

2. Material and methods

For the fabrication of single-phase Be₁₂Ti and Be₁₇Ti₂ samples, a combinatorial process, involving annealing of mixed starting powders for homogenization and plasma sintering, was employed. Beryllium and titanium powders of high purities (99.5% and 99.9%, respectively) and particle sizes of less than 45 μm, were mixed at concentrations of 92.3 atom% Be and 7.7 atom% Ti for Be₁₂Ti and 89.5 at.% Be and 10.5 at.% Ti for Be₁₇Ti₂, using a mortar (RM200, Retsch, Germany) for 1 h. Each of the mixed powders was heat-treated at 1473 K for 10 h in an alumina crucible (with purity of 99.9%) under Ar gas flow (300 ml/min). To crush the slightly consolidated powders, pulverization was carried out for 1 h using a mortar. Plasma sintering was performed on this powders at 1123 K. Sintering was carried out at holding times of 20 min with heating and cooling rates of 100 K/min and 200 K/min, respectively.

For qualitative analyses, the samples were cut into 4 × 4 × 5 mm strips and mechanically polished up to 15 μm. The samples were then characterized using x-ray diffraction profiles (XRD, UltimaIV, Rigaku, Japan) and electron probe microanalysis (EPMA, JXA-8530F, JEOL, Japan). To investigate the sintering density of the beryllide, including open porosity, the Archimedes immersion method and a He gas pycnometer (AccupycII 1340-1CC, Shimadzu, Japan) were used. Besides, Vickers micro-hardness was evaluated under a load with 9.807 N (measured 10 times and the values averaged).

Since the beryllide synthesis process includes heat treatment at high temperature, introduction of oxygen impurity is unavoidable. Accordingly, the concentration of oxygen in the samples was investigated using a gas elemental analyzer (ONH836, LECO, USA). The weight gain and the amount of generated H₂ for single-phase Be₁₂Ti and Be₁₇Ti₂ samples were evaluated using thermogravimetry (TG, TG-8110, Rigaku, Japan) at 1073, 1273, and 1473 K for 24 h in 15% H₂O/Ar. To investigate the thermal expansion, the coefficient of thermal expansion (CTE, TA5010SE, Netzsch) was conducted. For the evaluation of hydrogen isotope retention, thermal desorption

spectroscopy (TDS) test was carried out using the D⁺ irradiated beryllides, irradiated with 3 keV-D₂⁺ ion and fluence from 1 × 10²¹ to 1 × 10²³ ions/m².

3. Results and discussion

3.1. Synthesis of the single-phase beryllides

Through an iterative process, with respect to temperature and time for homogenization and sintering [1,4,5], single-phase Be₁₂Ti and Be₁₇Ti₂ beryllides were successfully fabricated as shown in Fig. 1. As seen from Fig. 1, both Be₁₂Ti and Be₁₇Ti₂ consist of a single phase, while there is a relatively high fraction of pores. Unlike plasma-sintered Be (Be: 1560 K) block [11], beryllides have relatively high melting points (Be₁₂Ti: 1868 K, Be₁₇Ti₂: 1903 K) and therefore require high sintering temperatures. However, the sintering conditions were similar to that of the Be sample. It is likely that the insufficient temperature leads to a relatively high porosity compared to plasma-sintered Be sample. However, point and area analyses using the wavelength dispersive spectroscopy (WDS) shows that the samples consisted of single phase.

Additionally, x-ray diffraction patterns clearly revealed the formation of single-phase beryllides (Fig. 2). Negligibly small peaks corresponding to impurities (such as Be oxide) exist, unavoidably formed during the homogenization treatment at 1473 K. Nevertheless, it is evident that most of the peaks indicate single-phase Be₁₂Ti and Be₁₇Ti₂, while the oxide moiety was also observed with considerably small peaks. This is in good agreement with the WDS analytical results.

3.2. Sinterability

Plasma sintering has attracted widespread interest because of its extensive application. Sinterability is one of the most important factors to be considered during the sintering process because it can be varied according to the required conditions.

To investigate the fundamental properties of the beryllides, sinterability was evaluated using density measurement based on water immersion and a He pycnometer.

Fig. 3 shows the density and porosity of the Be₁₂Ti and Be₁₇Ti₂ beryllides. Our results suggest that the synthesized beryllides have a lower relative density and higher porosity than Be [11] and other beryllides [9]. It is well known that the fabrication method and the sintering conditions can result in different sintering densities and porosities. Since Be powder has ductility, whereas homogenized beryllides powders are considerably brittle, the plasma-sintered Be and beryllides showed different values. In addition to this, applying a common sintering temperature led to a difference in the density and porosity. Significantly, there was no difference between the synthesized beryllides.

The Vickers hardness of Be₁₂Ti and Be₁₇Ti₂ was measured as shown in Fig. 4. As mentioned in the previous study [12], hardness of each phase in the plasma-sintered Be-7.7 atom% Ti beryllides consisting of Be, Be₁₂Ti, Be₁₇Ti₂, and Be₂Ti were evaluated. The hardness of Be₁₂Ti and Be₁₇Ti₂ were 370 and 560 Hv, respectively, which is considerably lower than those in the previous study (1280 and 1380 Hv). Since the sintering in the present study was performed at a lower temperature (1123 K vs. 1273 K in the previous study), it is possible that the sintering resulted in a lower consolidation of the compounds, and therefore the hardness of Be₁₂Ti and Be₁₇Ti₂ are considerably low.

Although homogenization treatment at 1473 K for 10 h was carried out under Ar flow (300 ml/min) after evacuation of up to 1 × 10⁻⁴ Pa, oxidation of the mixed powders was unavoidable. Oxygen concentration in general metals not only contributes to the

Download English Version:

<https://daneshyari.com/en/article/5457646>

Download Persian Version:

<https://daneshyari.com/article/5457646>

[Daneshyari.com](https://daneshyari.com)