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Hydrogen generation property on the surface of plasma sintered $Be_{12}Ti$

Kohei WADA[1], Kenzo MUNAKATA[1], Yusuke AKIMOTO[1], Haruki TAKEDA[1],
Jae-Hwan KIM[2], Daisuke WAKAI[2],Kazuo YONEHARA[2] and Masaru Nakamichi[2]

[1]*Faculty of engineering and resource science, Akita university, 1-1, Tegatagakuen-cho, Akita, 010-8502, Japan*
[2]*Fusion Research and Development Directorate, Japan Atomic Energy Agency, 2-166, Omotedate, Obuchi, Rokkasho, Kamikita, Aomori, 039-3212, Japan*

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Central and peripheral parts of a plasma sintered titanium beryllide disc were exposed to water vapor at temperature rising up to 1273 K. Hydrogen generation on and oxidation properties of the titanium beryllide ~~surfaces~~ were investigated. According to electron probe microanalysis, the titanium beryllide parts were characterized by different surface area fractions of Be, $Be_{12}Ti$, $Be_{17}Ti_2$, and Be_2Ti phases, and the central part contained lower fraction of Be phase than the peripheral part. H_2 gas generation rate in the central part was found to be lower than that in the peripheral part, and this difference can be attributed to larger fraction of the Be phase. Secondary electron microscopy and X-ray diffraction revealed that the parts of the plasma sintered $Be_{12}Ti$ disc had higher oxidation resistance than metallic beryllium.

Keywords: beryllide, plasma sintering, hydrogen generation, oxidation, gas chromatograhphy

1. Introduction

Metallic beryllium has been considered as a leading candidate for a neutron multiplier in water- or helium-cooled solid breeder blankets in future fusion reactors. In these blankets, beryllium will be subjected to a high neutron flux and located in high temperature environment. However, beryllium is highly reactive with water vapor at temperatures above 873 K, producing hydrogen that may lead to accidents due to H_2 gas explosion.

$$Be + H_2O = BeO + H_2 \qquad (1)$$

Titanium beryllides such as $Be_{12}Ti$ have many advantages over beryllium from the perspectives of higher melting point, lower chemical reactivity, lower swelling, etc. Therefore, $Be_{12}Ti$ material has attracted attention as an alternative of beryllium, and could be used as an advanced neutron multiplier in the fusion reactor blankets [1].

Titanium beryllides have been fabricated by various methods. Nakamichi et al. [2, 3] have developed new synthesis process of $Be_{12}Ti$ material called "plasma-sintering method". This process consists of loading raw material powder in the punch and the die unit, direct current pulse plasma generation to activate the surface of powder particles, and uniaxial pressing to enhance the sinterability [2,3].

In this study, we report results on H_2 generation caused by interaction of water vapor with titanium beryllides. Besides, oxidation resistance of the titanium beryllides with slightly different phase compositions was studied.

2. Experimental

Be and Ti powders, characterized by average grain sizes of 27 μm and 28 μm, respectively, were mixed for 60 min by using a mortar grinder RM200 (Retsch, Germany). The mixed ratio was adjusted to the stoichiometric composition of $Be_{12}Ti$ (69.3:30.7 wt.%). The mixed powder was placed in a plasma electrical discharge sintering device KE-PAS III (manufactured by KAKEN Co. Ltd), and $Be_{12}Ti$ disc, 20

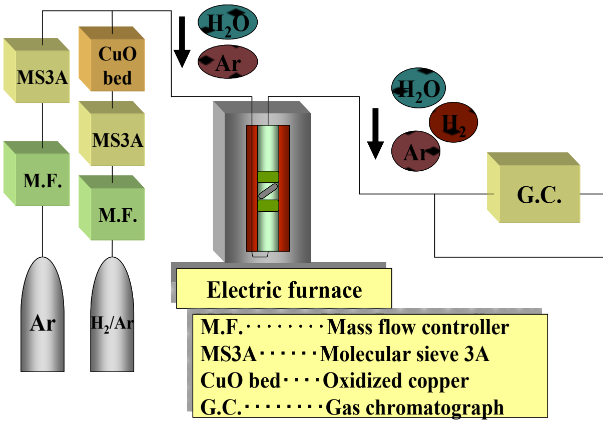

Fig. 1 Schematic flow diagram of test apparatus.

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authors e-mail : *kohei.wada1986@gmail.com* mm in diameter and 5 mm in thickness, was synthesized by sintering for 40 min at a temperature of 1273 K and a pressure of 50 MPa. Then the disc was cut into two small samples to separate central and peripheral parts of the disc for comparative analyses. The surface area of the central parts was 83 mm^2 while that of the peripheral part was 128 mm^2. The samples were mechanically polished with a #2400 SiC abrasive paper.

The surface morphology of the $Be_{12}Ti$ samples was examined by secondary electron microscopy (SEM) combined with the electron probe microanalysis (EPMA) in a SEM/EPMA instrument JXA-8230 (JEOL Co.)

Schematic flow diagram of apparatus for a measurement of the hydrogen generation rate is shown in Fig. 1. The $Be_{12}Ti$ sample was wrapped by platinum mesh to avoid direct contact with the test tube, and then placed between silica wools. 10,000 ppm H_2O/Ar gas was generated by passing 10,000 ppm H_2 /Ar gas through copper oxide bed heated at 623 K, and then introduced to the test tube with a flow rate of 300 cm^3/min. An electric furnace was used to heat the test tube at a heating rate of 5 K/min, and a temperature inside the tube was raised up to 1273 K. This temperature was kept constant until hydrogen generation terminated.

The concentrations of hydrogen in the outlet streams of the reactor were measured with a gas chromatograph GC-8A manufactured by SHIMADZU Co. The state of oxidized sample surface was characterized by X-ray diffraction (XRD) analysis with the Ultima IV instrument (RIGAKU Co.) and electron probe micro analysis (EPMA) with the SEM/EPMA JXA-8230 instrument (JEPL Co.).

3. Result and discussion

Figure 2 shows the SEM images using back-scattered electron for central and peripheral parts of the plasma sintered titanium beryllide disc prepared in this study. The results of EPMA analysis demonstrated that the titanium beryllide is composed of four different phases such as Be, $Be_{12}Ti$, $Be_{17}Ti_2$, and Be_2Ti with different fractions. Percentages of the surface areas of the phases for each part of the disc, evaluated with the use of an image analyzer, are shown in Table 1. It is evident that the central part is composed mainly of $Be_{12}Ti$ phase with relatively large fraction of $Be_{17}Ti_2$ phase. Additionally, smaller fractions of Be and $Be_{12}Ti$ phases were observed. Note that phase compositions for the central and peripheral parts were slightly different. This observation is in good agreement with results obtained by Kim et al. [4] proposing that the phase difference for the central and peripheral parts can be explained by a temperature gradient maintained during the sintering process.

Experiments on generation of H_2 gas on the surfaces of the plasma sintered titanium beryllides were carried out to investigate the effect of the phase composition. Fig. 3 shows changes in hydrogen concentrations in the outlet stream of reactor with central and peripheral part of the plasma sintered titanium beryllide disc exposed to a 10,000 ppm H_2O/Ar gas. In case of the central part, generation of hydrogen started at a temperature of 673 K and continued for about 27 h. The total amount of hydrogen generated for 24 h is 1.2×10^{-4} mol/cm^2. For the peripheral part, however, the hydrogen generation started at a temperature above 423 K and continued for 40 hr. The total amount of hydrogen generated on the peripheral part for 24 h is 3.0×10^{-4} mol/cm^2. As mentioned above, the samples used in this work included the phase of Be_2Ti (Table 1) that is known to

Table 1 Surface area fractions (in %) of phases constituent central and peripheral parts of titanium beryllide disc.

	Beryllide (a) (%)	Beryllide (b) (%)
Be	0.96	2.53
$Be_{12}Ti$	89.40	90.8
$Be_{17}Ti_2$	8.16	5.87
Be_2Ti	1.88	1.25

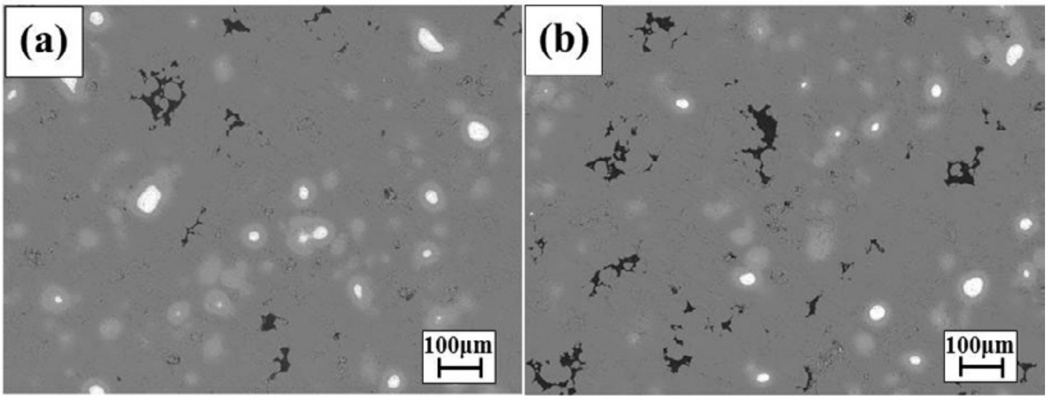

Fig. 2 SEM images of central part (a) and peripheral part (b) of plasma sintered titanium beryllide disc.

have capability of hydrogen storage [5]. The existence of this phase might affect the hydrogen generation of the samples, while the fractions of the phase in the both samples were almost the same. The Be$_{17}$Ti$_2$ phase could also affect the hydrogen generation, but this phase is probably stable and tolerant to oxidation as much as the Be$_{12}$Ti phase [Kim paper Numat]. Thus, it is thought that the sample with larger fraction of Be phase generates more amounts of H$_{2,}$ since Be is known as highly reactive with oxygen [6] and water vapor [7]. As shown in the EPMA analysis (Table 1), the edge sample was composed of larger fraction of Be, which affect the amount of generated H$_2$ gas. This agrees with the report by Anderl et al. [8], demonstrating that the rate of the reaction between beryllium surface and water vapor is associated with differences in the specific surface areas for the tested materials.

The weight gain for the Be$_{12}$Ti and beryllium samples indicate that the center sample part increased by 3.6 % of the initial weight for the central part of the titanium beryllide and 4.7 % for the peripheral part. However, as reported in our previous study [9], for metallic beryllium used as a reference material, the weight gain was 50 % of the initial weight. Data on the weight gain and amount of generated hydrogen for the titanium beryllide parts indicate that the peripheral part is more oxidized.

SEM observation and XRD analysis were performed to investigate the surface state of the two samples after exposure to 10,000 ppm H$_2$O/Ar gas. Fig. 4 shows the SEM images of central (a) and peripheral (b) parts of the plasma sintered titanium beryllide disc and metallic beryllium (c) after exposure to water vapor. The Be sample (shown in Fig. 4 (c)) was used in our previous work and the surface of the sample was observed using the SEM/EPMA apparatus [9]. The result of the SEM analysis clarified that after oxidation the surfaces of the titanium beryllide parts are covered with dense and protective oxide scales (see Fig. 4 (a) and (b)). Gray and white areas in the SEM pictures correspond to BeO and TiO$_2$, respectively. Comparison of the oxidation behavior of Be$_{12}$Ti and beryllium metal indicate that more protective BeO scales are present on the surface of the Be$_{12}$Ti sample parts. In contrast, it could be stated that metallic Be possesses poor oxidation resistance due to cracked and fractured BeO scales present of the surface. Sato et al. [10] had demonstrated that BeO formed on the surface of metallic Be is affected by compressive stress caused by coherency of the lattice structures between the scale and the bulk metal, since the atomic distances in the BeO scale are smaller than those in the metallic Be substrate.

The results of the XRD analysis (Fig. 5) demonstrated that the intensity of peaks corresponding to BeO formed on the peripheral part are higher than those for the central part. This is in good agreement with the result of the weight gain

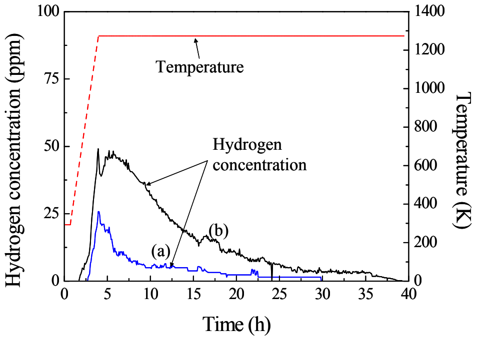

Fig. 3 Change in concentration of hydrogen in the outlet stream of reactor with central part (a) and peripheral part (b) of the plasma sintered titanium beryllide disc exposed to a 10 000 ppm H$_2$O/Ar gas.

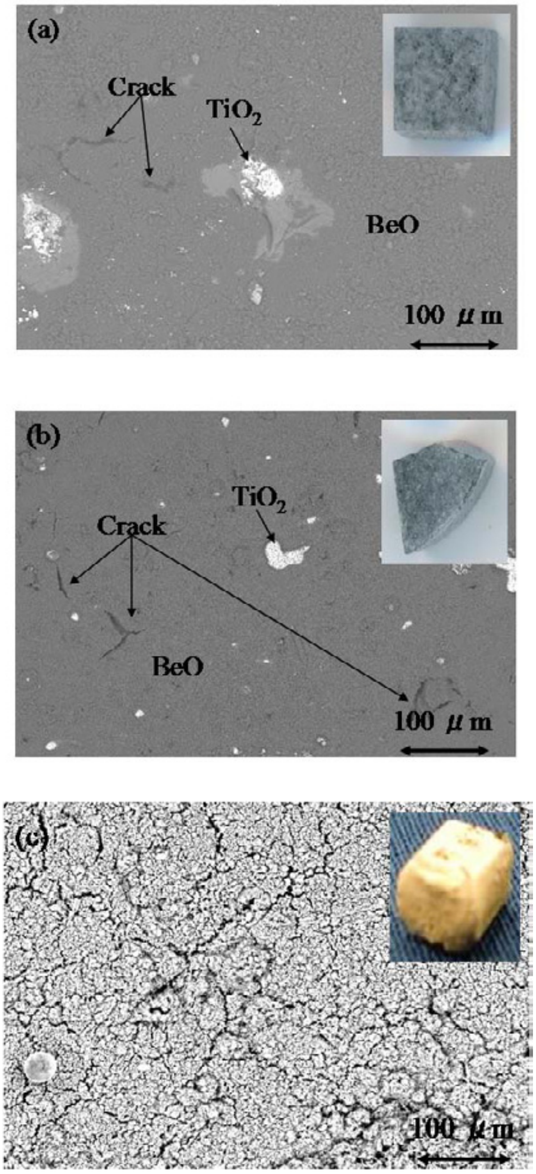

Fig. 4 SEM images of central (a) and peripheral (b) parts of the plasma sintered titanium beryllide disc and metallic beryllium [8] (c) after exposure to water vapor.

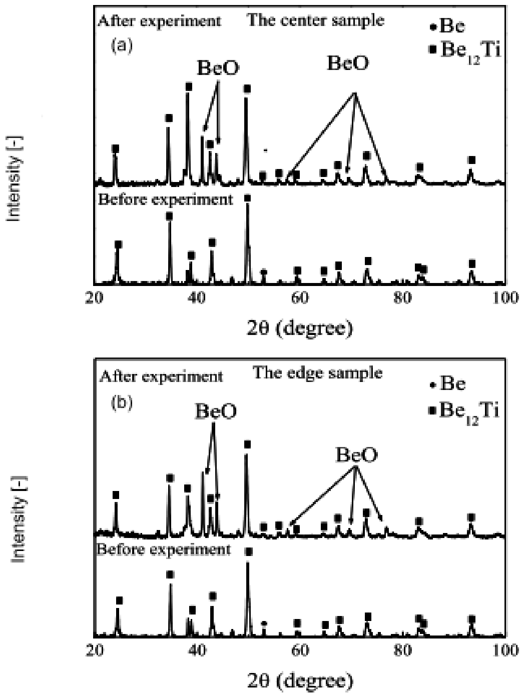

Fig. 5 XRD spectra of central (a) and peripheral (b) parts of the plasma sintered titanium beryllide disc after exposure to water vapor.

and H_2 gas generation. These results obviously suggest that the oxidation resistance for the central sample part of the plasma sintered beryllide disc is higher than that for the peripheral part. Therefore, as mentioned above, larger fraction of highly reactive Be in the titanium beryllide leads (i) to increase in the amount of H_2 gas generated under exposure to water vapor and (ii) to poor oxidation resistance of the surface.

4. Conclusion

Center and peripheral parts (with different surface area fractions of Be, $Be_{12}Ti$, $Be_{17}Ti_2$, and Be_2Ti phases) were cut and extracted from a plasma sintered $Be_{12}Ti$ disk in order to investigate the effect of the surface area fraction difference on not only the H_2 gas generation under exposure to water vapor but also oxidation property. It has been shown that the amount of hydrogen generated for the surface of the central part of the titanium beryllide disc was smaller than that for the peripheral part. This difference can be explained by lower fraction of the Be phase surface area on the surface of the central part in comparison with that for the peripheral part. The oxidation property for both parts did not exhibit big difference, while both titanium beryllides parts demonstrated higher oxidation resistance compared to metallic beryllium.

5. Acknowledgments

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6. References

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