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Interaction of titanium beryllide with steam at high temperatures

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HIGHLIGHTS

- Some central and peripheral parts of a plasma sintered titanium beryllide disk were exposed to water vapor at 1273 K.
- H_2 gas generation rate of the central part was found to be lower than that of the peripheral part.
- Central parts of a plasma sintered titanium beryllide disk were exposed to water vapor at 1273 K with different temperature controls.
- H_2 gas generation was found to be affected by thermal treatment.

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ABSTRACT

Some central and peripheral parts of a plasma sintered titanium beryllide disk were exposed to water vapor at temperatures raised up to 1273 K. Hydrogen generation and oxidation properties of the titanium beryllide were investigated. The amount of H_2 generation of the central part was found to be smaller than that of the peripheral part, and this can be attributed to difference in the larger fractions of the Be phase on their surface. Thus, different temperature programed experiments were performed using samples cut out from the central part. In an experiment, the temperature of the sample was raised stepwise and behavior of hydrogen generation was investigated. It was found that hydrogen generation does not take place at the temperatures below 1273 K and the amount of hydrogen generated is far smaller. Another experiment was carried out after a sample had been annealed under a dry Ar gas at 1273 K. In this case, the amount of hydrogen generated from the surface decreased. These results indicate the thermal treatment of the titanium beryllide samples affects their reactivity with water vapor.

1. Introduction

Metallic beryllium has been considered as a leading candidate material for the neutron multiplier in water or helium cooled solid breeder blankets of 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 high temperatures, which produces explosive hydrogen.

Titanium beryllides such as $Be_{12}Ti$ have some advantages over beryllium from the perspectives of higher melting point, lower chemical reactivity, lower swelling and so forth. Therefore, $Be_{12}Ti$ is attracting attention as an alternative of beryllium, and would be used as an advanced neutron multiplier in the fusion reactor blankets [1].

Titanium beryllides have been fabricated by various methods. For example, oxidation behavior of the $Be_{12}Ti$ samples prepared by the HIP method was previously studied by Munakata et al. [2–4]. More recently, Nakamichi et al. [5,6] have developed new synthesis process of $Be_{12}Ti$ material called "plasma-sintering method". This process consists of (1) loading of raw material powder in the punch and the die unit, (2) direct current pulse plasma generation to activate the surface of powder particles, and (3) uniaxial pressing to enhance their sinterability.

In this work, we studied H_2 generation caused by interaction of water vapor with titanium beryllides. Besides, we investigated oxidation resistance of the titanium beryllides with slightly different phase compositions. Furthermore, different temperature programmed experiments were performed to investigate the effect of thermal treatment on reactivity of the samples with water vapor.

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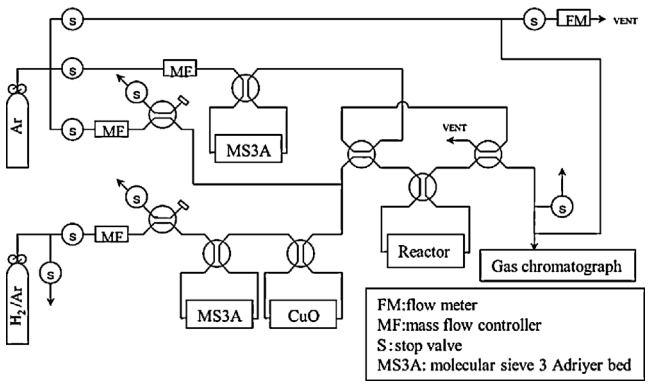

Fig. 1. Schematic flow diagram of test apparatus.

2. Experimental

Be and Ti powders 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 a $Be_{12}Ti$ disk with 20 mm in diameter and 5 mm in thickness, was synthesized by sintering for 40 min at a temperature of 1273 K and under pressure of 50 MPa. Then, the disk was cut into several small samples such as central (sample A) and peripheral (sample B) parts 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.

Quantitative surface analysis of the $Be_{12}Ti$ samples was performed by secondary electron microscopy (SEM) combined with the electron probe microanalysis (EPMA, JXA-8230, JEOL Co.). The area fractions of each phase were evaluated by ImageJ software (IamgeJ 1.44p, National Institutes of Health, USA), gathering average date after several measurements.

A Schematic flow diagram of apparatus for a measurement of the hydrogen generation is shown in Fig. 1. The $Be_{12}Ti$ samples were wrapped with a platinum mesh to avoid direct contact of the samples with the test tube made of quartz, and they were placed between silica wools. 10,000 ppm H_2O/Ar gas was generated by passing 10,000 ppm H_2/Ar gas through a copper oxide bed heated at 623 K, which was introduced to the test tube with a flow rate of 300 cm^3/min. An electric furnace was used to heat the test tube. In the first two experiments, the test tube was heated at the ramp rate of 5 K/min, and a temperature inside the tube was finally raised up to 1273 K. This temperature was kept constant until hydrogen generation terminated. In the other experiments, the temperature of the test tube was raised stepwise up to 1273 K. During the period of raising the test tube temperature, a dry Ar gas was passed through the test tube. The dry Ar gas was prepared using a molecular-sieve 3A (MS3A) adsorbent bed to remove several tens ppm of residual water vapor contained in the Ar gas supplied from gas cylinders.

3. Result and discussion

3.1. Temperature programed experiments with constant ramp rate

As mentioned above, in the first two experiments, the test tube was heated at the rate of 5 K/min, and a temperature inside the tube was finally raised up to 1273 K. More details of the experiments and detailed surface analysis can be cited in our previous report [7]. Thus, hereafter the main experimental results are summarized. Fig. 2 shows changes in hydrogen concentrations in the outlet stream of reactor with central (sample A) and peripheral (sample B) part of the plasma sintered titanium beryllide disk exposed to a 10,000 ppm H_2O/Ar gas. This figure shows change in the test tube temperature and variation in the integrated total amounts of hydrogen generated, as well. In the 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 was 1.3×10^{-4} mol/cm^2. For the peripheral part, however, the hydrogen generation started at a temperature above 423 K and continued for 40 h. The total amount of hydrogen generated from the peripheral part for 24 h was 3.3×10^{-4} mol/cm^2. Experiments on pure beryllium were performed by other authors, of which data can be used for comparison [8]. Table 1 shows the surface area fractions of phases in the central (sample A) and peripheral (sample B) parts of titanium beryllide disk. As seen in this table, the samples used in this work included the phase of Be_2Ti that is known to have capability of hydrogen storage. The existence of this phase might affect the hydrogen generation of the samples, while the fractions of the phase in both samples are almost the same. The $Be_{17}Ti_2$ phase

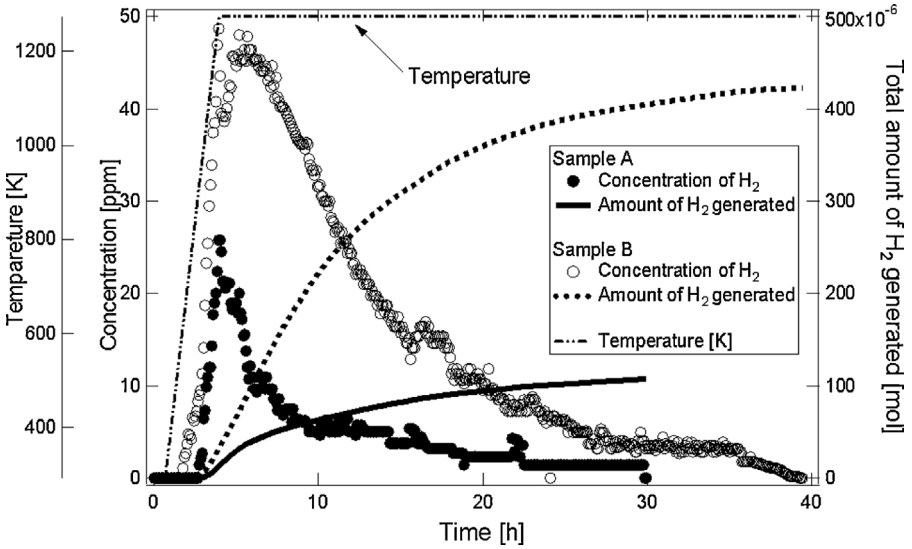

Fig. 2. Change in concentration of hydrogen in the outlet stream of reactor with central part (sample A) and peripheral part (sample B) of the plasma sintered titanium beryllide disk exposed to a 10,000 ppm H_2O/Ar gas.