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Stability of titanium beryllide under water vapor

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Abstract

Titanium beryllides such as $Be_{12}Ti$ are considered to be promising alternatives to beryllium as the neutron multiplier. Thus, the authors investigated the reactivity of $Be_{12}Ti$ with water vapor. In the experiments, the $Be_{12}Ti$ sample was exposed to a gas containing water vapor of 10 000 ppm at temperatures as high as 1000 °C. Chaotic breakaway reactions were not observed for the $Be_{12}Ti$ sample, and the amount of hydrogen generated was found to be far smaller in comparison with beryllium. Thus, it can be said that $Be_{12}Ti$ is less reactive with water vapor, which is a great merit for the neutron multiplier.

1. Introduction

In most current designs of D–T fusion reactors, beryllium is regarded as the most promising candidate material as the neutron multiplier in the tritium-breeding blanket, needed to increase the tritium-breeding ratio. For the instance, in the blanket designs for a prototype reactor with water or helium coolant, beryllium is used in the form of a pebble bed. In these blanket designs, beryllium could be located in a high neutron flux and high temperature environment. Thus, concerns with the use of beryllium include the compatibility with structural materials, the tritium inventory, and the reactivity of beryllium with water vapor or oxygen.

Titanium beryllides such as $Be_{12}Ti$ are known to have advantages over beryllium from the perspectives of higher melting point, lower chemical reactivity, lower swelling, etc. Therefore, there is a probability that these materials are promising alternatives of beryllium. At present, few experimental data are available for these materials, and thus more experimental studies need to be done to evaluate their performance as the neutron multiplier.

With respect to the reaction with water vapor, beryllium is known to be highly reactive especially at high temperatures and under high vapor pressures of water vapor, which produces hydrogen via the following reaction [1–4].

$$Be + H_2O \rightarrow BeO + H_2$$

This is one of the major drawbacks of using beryllium, which poses a threat to the safety of the fusion power plant particularly in the case of a loss-of-coolant accident (LOCA) in which a water-line break injects steam into the blanket. Therefore, in this work, the authors investigated the reactivity of $Be_{12}Ti$, one of the titanium beryllides, with water vapor.

2. Experimental

The sample disk of $Be_{12}Ti$ was prepared by NGK INSULATORS LTD., and its geometry was 7.9 mm in diameter and 1.4 mm in thickness. An ingot of $Be_{12}Ti$ was fabricated from beryllium and titanium powders by the HIP process. It was machined to the disk shape of

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which surface was mirror-polished. The sample was used as received in the experiment, and neither chemical treatment nor conditioning was attempted. Before use, the surface of the sample had a metallic luster. The chemical composition of the sample is listed in Table 1.

The experiments on the chemical stability of $Be_{12}Ti$ under water vapor were conducted using an experimental apparatus shown in Fig. 1. The reactor consists of a quartz tube, of which temperature was controlled with a conventional electric furnace and a temperature controller. The sample disk of $Be_{12}Ti$ wrapped with a platinum mesh sheet (2.5 cm × 2.5 cm, 52 meshes per inch) was placed in the reactor. The sample disks were wrapped with the platinum mesh sheet to avoid direct contact of the samples with the quarts tube reactor, since quartz is reactive with titanium beryllides at higher temperatures. An argon gas containing a certain amount of water vapor was introduced to the reactor. The concentrations of hydrogen and water vapor in the inlet and outlet streams of the reactor were measured with a quadrupole mass spectrometer (Mini-Lab MKS). The gases employed were purified with molecular sieve 3A beds to remove water vapor in the process gas. Water vapor in the process was generated by passing a H_2/Ar gas to a copper oxide bed held at 350 °C. The temperature of the reactor was raised at the constant rate up to the test temperatures and then held constant.

Table 1
Chemical composition of $Be_{12}Ti$ sample

Element	wt%
Be	Balance
BeO	1.32
Mg	0.001
Al	0.014
Si	0.025
Ti	33.4
Cr	0.003
Fe	0.044
Co	0.047
Ni	<0.001
Cu	<0.004
W	<0.01
C	0.026

3. Results and discussion

In the reaction of beryllium with water vapor, it is known that a chaotic breakaway reaction takes place at high temperatures and high water vapor pressures; the reaction appears to be autocatalytic and considerable amounts of beryllium react with water vapor, which makes the surface of the beryllium sample crumby [2,3]. The results of previous studies indicate that such a breakaway reaction takes place at temperatures higher than 700 °C and water vapor concentrations as low as 1000 ppm [1,2]. With reference to the previous results, the authors first tested the chemical stability of $Be_{12}Ti$ under water vapor of about 1000 ppm. Fig. 2 shows the change in the concentrations of water vapor (broken line) and hydrogen (solid line) in the outlet stream of the reactor when the argon gas containing 960 ppm of water vapor was introduced. The chained line in the figure shows the change in the reactor temperature. The flow rate of the gas was 91.6 cm^3-STP/min. First, the reactor temperature was held at ambient temperature for 30 min, and then it was raised to 940 °C at the constant rate of 10 °C/min. As seen in Fig. 2, at low temperatures, no hydrogen was observed in the outlet stream of the reactor. However, the generation of hydrogen started at a temperature near 400 °C. After this, the concentration of hydrogen continued to increase and reached a peak at 870 °C. Then, the concentration of hydrogen began to

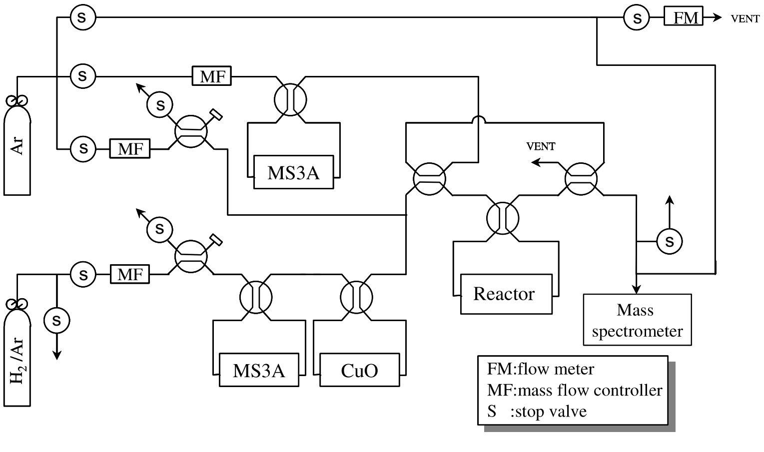

Fig. 1. Experimental apparatus.

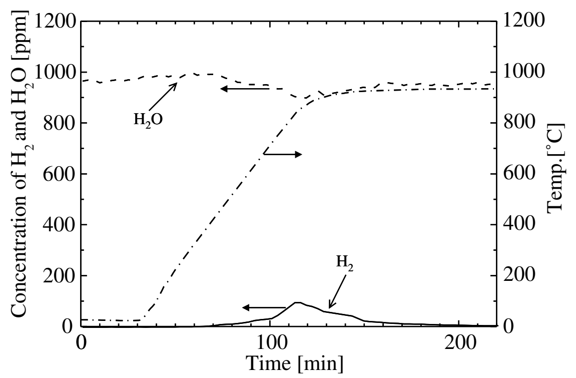

Fig. 2. Change in the concentration of water vapor and hydrogen in the outlet stream of the reactor charged with a $Be_{12}Ti$ disk exposed to a 960 ppm H_2O/Ar gas.

decrease and the generation of hydrogen terminated at 220 min after the commencement of the experiment. After the experiment, the surface of the sample disk had lost the metallic luster to some extent, but appreciable weight change was not observed. Furthermore, the result of this work reveals that a breakaway reaction, which has been reported to take place on the surface of beryllium, does not take place on the surface of the $Be_{12}Ti$ disk even at 940 °C under the presence of 960 ppm of water vapor.

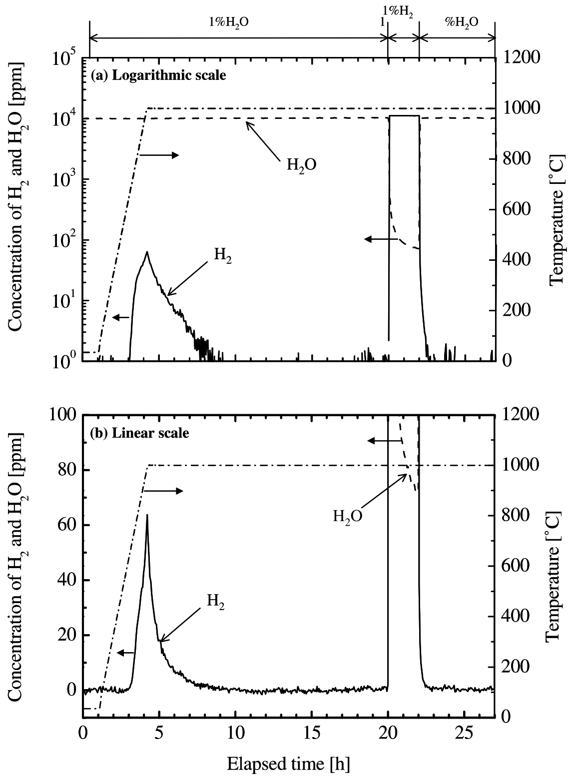

Fig. 3. Change in the concentration of water vapor and hydrogen in the outlet stream of reactor with a $Be_{12}Ti$ disk exposed to a 10 000 ppm H_2O/Ar gas ((a) logarithmic scale, (b) linear scale).

With the encouraging result shown above, the authors next investigated the chemical stability of $Be_{12}Ti$ under water vapor of 10 000 ppm (1%). According to the previous results [1,2], the chaotic breakaway reaction unquestionably takes place on the surface of beryllium under 10 000 ppm of water vapor at high temperatures. Fig. 3(a) and (b) show the changes in the concentrations of water vapor and hydrogen in the outlet stream of the reactor when the argon gas containing 10 000 ppm of water vapor was introduced. The chained line in the figure shows the change in the reactor temperature. The flow rate of the gas was 84.9 cm^2-STP /min. First, the reactor temperature was held at ambient temperature for 1 h, and then it was raised up to 1000 °C at the constant rate of 5 °C/min; in this experiment, the temperature ramp was decreased. A dry argon gas was introduced to the reactor for the initial 30 min, then the gas introduced was changed to the gas containing 10 000 ppm of water vapor; the gas composition in the figure for initial 30 min correspond to the inlet gas composition. At low temperatures, no hydrogen appeared in the outlet stream of the reactor. The generation of hydrogen started at a temperature near 600 °C, and the concentration of hydrogen in the outlet stream of the reactor reached a peak at 1000 °C. Then, the concentration of hydrogen began to decrease and the generation of hydrogen terminated at 10 h after the commencement of the experiment, but the reactivity test of the sample was still continued to confirm the durability of $Be_{12}Ti$ to water vapor. However, further hydrogen generation or breakaway reaction was not observed. In total, the sample was exposed to 10 000 ppm of water vapor for 15 h at the temperature of 1000 °C. The gas introduced to the reactor was changed to a 10 000 ppm H_2/Ar gas at 20 h after the commencement of the experiment to observe whether the reduction of the surface of the sample takes place under the presence of hydrogen. Since we have only the measurement of the concentration of water vapor, it is difficult to determine whether any reduction takes place, since changes in water vapor concentrations usually include delay after the high water vapor concentration is abruptly decreased; this delay takes place due to the gradual desorption of water from the piping system. Thus, the process gas was again changed to the 10 000 ppm H_2O/Ar gas at 22 h after the commencement of the experiment, and then the concentration of hydrogen was traced. However, appreciable hydrogen generation was not observed as shown in Fig. 3(b). This result suggests that the oxidized state of the surface of the sample is stable. After the experiment, the color of the surface of the sample disk was found to turn to white

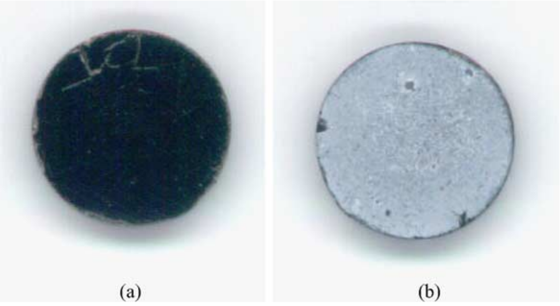

Fig. 4. Photographs of a $Be_{12}Ti$ sample: (a) before and (b) after experiment.

(see Fig. 4), which could indicate that the surface of the sample was covered by the layer of beryllium oxidized. The weight gain between before and after the experiment was 0.8 mg, which is 0.5% of the initial weight of the disk sample (153.51 mg). The weight gain per unit surface was estimated to be 0.29 mg/cm^2. In the case of beryllium, a further drastic weight gain based on the breakaway reaction starts when the weight gain exceeds approximately 0.1 mg/cm^2, and the weight gain appears to exceed 20 mg/cm^2 at temperatures as low as 750 °C [2]. Therefore, the amount of oxidized $Be_{12}Ti$ is far smaller in comparison with the case of beryllium.

Anderl et al. [4] have reported that the rate of the reaction between beryllium surface and water vapor can be accounted for by differences in the specific surface areas for the tested materials. Their result indicates that the hydrogen generation rate at the temperature of 1000 °C is about 0.13 $mol/m^2\,s$. Note that the hydrogen generation rates reported by them are averaged values over entire experimental periods. The hydrogen generation rate on the surface of the $Be_{12}Ti$ sample was estimated using the value of peak hydrogen generation rate at 1000 °C shown in Fig. 3(b). The hydrogen generation rate was calculated be 3×10^{-5} $mol/m^2\,s$ on the basis of the geometrical surface area of the sample. Comparison of these values suggests that the hydrogen generation rate for the $Be_{12}Ti$ sample is, at least, approximately 4000 times smaller than that for beryllium at this temperature. Therefore, it can be said that $Be_{12}Ti$ is far less reactive with water vapor, which is a great merit for the neutron multiplier of fusion power plants.

4. Conclusion

The chemical stability of $Be_{12}Ti$ under water vapor was investigated using disk samples of $Be_{12}Ti$. In the experiments, the $Be_{12}Ti$ sample was exposed to a gas containing water vapor of 10 000 ppm at temperatures as high as 1000 °C. Chaotic breakaway reactions were not observed for the $Be_{12}Ti$ sample and the amount of hydrogen generated was found to be far smaller than for beryllium under similar conditions. Thus, it can be said that $Be_{12}Ti$ is far less reactive with water vapor than is beryllium.

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