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Kinetics of reaction with water vapor and ab initio study of titanium beryllide

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Abstract

Beryllium is one of the candidate materials of the neutron multiplier in the tritium-breeding blanket. 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 and so forth. The reaction of titanium beryllides with water vapor was investigated. The sample disks of $Be_{12}Ti$ were exposed to an argon gas with 10000 ppm of water vapor, and the sample temperature was raised to 1000 °C. However, the chaotic breakaway reaction was not observed. The kinetics of oxidation on the surface of $Be_{12}Ti$ by water vapor was investigated using a model differential equation, and the reaction constant was quantified. Furthermore, to know the electron state in $Be_{12}Ti$, ab initio calculations of quantum chemistry were performed using CRYSTAL 98. The structure optimization of $Be_{12}Ti$ crystal was attempted, and an electron density map was generated.

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1. Introduction

Beryllium is one of the candidate materials of the neutron multiplier in the tritium-breeding blanket. In the D–T fusion blanket, beryllium would be placed in the high neutron flux and high temperature environment. Thus, there are some problems related to the application of beryllium as the neutron multiplier, which are the compatibility with structural materials, the tritium inventory and the reactivity of beryllium with water vapor and oxygen in the Loss of Coolant Accident (LOCA). Titanium beryllides such as $Be_{12}Ti$ are known to have advantages over beryllium from the perspectives of higher melting point, lower chemical reactivity and lower swelling. Thus, these materials are promising alternatives of beryllium. With regard to the reaction with water vapor, beryllium is known to be highly reactive at high temperatures and under high vapor pressures of water [1–3], which is one of the major drawbacks of beryllium. The authors investigated the reaction of titanium beryllides with water vapor at high temperatures [4]. The experimental results reveal that the amount of water, which reacts with $Be_{12}Ti$, is much smaller compared with beryllium.

It is necessary to know the generation rate of hydrogen when the interaction between water vapor and $Be_{12}Ti$ takes place. Thus, the kinetics of

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oxidation on the surface of $Be_{12}Ti$ by water vapor was investigated using a model differential equation. Recent advance in computer performance and computer codes makes it possible to study the chemical nature of substances by ab initio calculation that is a powerful tool to know how the electrons affect the property. Preliminary ab initio calculations of quantum chemistry were performed using CRYSTAL 98 to know the electron state in $Be_{12}Ti$.

2. Experimental

The sample disk (7.9 mm $\phi \times 1.4$ mm thick) of $Be_{12}Ti$ was prepared by NGK INSULATORS LTD. The sample was used as received in the experiment. Before use, the surface of the sample had a metallic luster. Details of the chemical composition of the sample have been reported in the previous literature [4].

The experiments on the chemical stability of $Be_{12}Ti$ under water vapor were conducted using an experimental apparatus shown in Fig. 1. 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 made of quartz. 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.

3. Overview of experimental result

In the reaction of beryllium with water vapor, it is known that a autocatalytic and chaotic breakaway reaction takes place at high temperatures and high water vapor pressures [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].

The authors investigated the chemical stability of $Be_{12}Ti$ under water vapor at a concentration of 10000 vppm (1%). Fig. 2 shows the changes in the concentration of hydrogen (which is the product of the reaction between H_2O and $Be_{12}Ti$) in the outlet stream of the reactor when the argon gas containing 10000 ppm of water vapor was introduced. The dashed line shows the change in the reactor temperature. The reactor temperature was raised up to 1000 °C at the constant rate of 5 °C/min. At low temperatures, no hydrogen appeared in the outlet stream of the reactor. The generation of hydrogen started at a temperature near 800 °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 start of the experiment. More details of the experimental results are reported in previous literature [4].

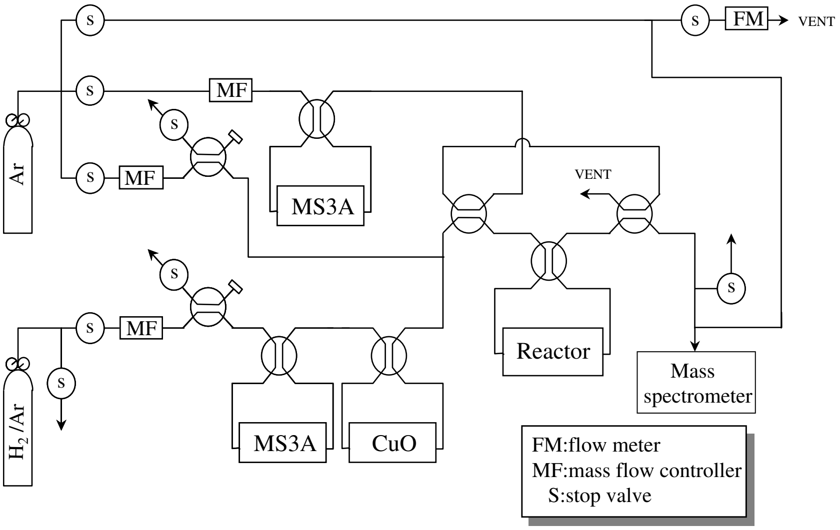

Fig. 1. Schematics of experimental apparatus (Water vapor in the process gas was generated by passing a H_2/Ar gas to a copper oxide bed held at 350 °C).

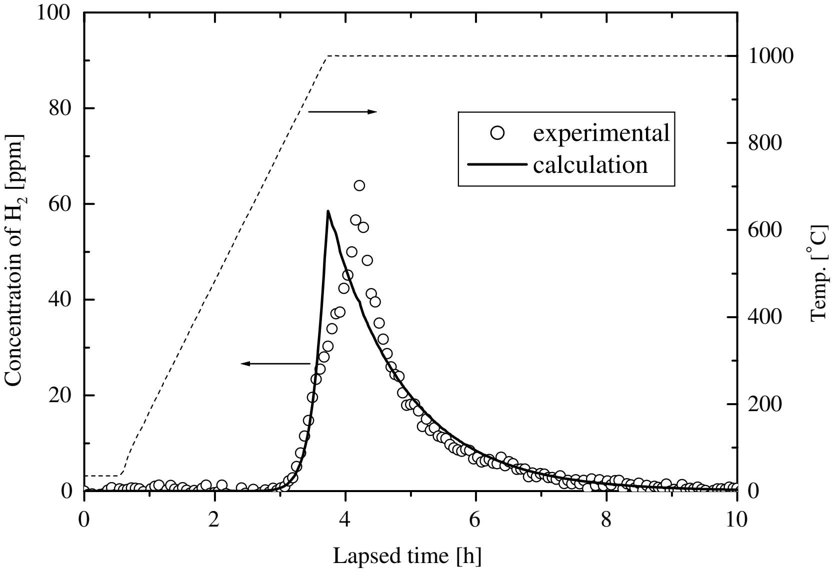

Fig. 2. Change in the concentration of hydrogen in the outlet stream of reactor with a $Be_{12}Ti$ disk exposed to a 1% H_2O/Ar gas (gas flow rate: 84.9 cm^3-STP /min).

After the experiment, the color of the surface of the sample disk was found to be white. The surface of the sample was observed using a digital microscope and a SEM. More detailed surface analysis was conducted using XRD and ESCA techniques as well. The results of the analysis revealed that the surface of the sample was oxidized and beryllium oxides appear to have been formed. However, titanium oxides were not observed. More details of the surface analysis are reported previously [5,6].

4. Analysis of kinetics of the surface reaction

The kinetics of oxidation on the surface of $Be_{12}Ti$ by water vapor was examined using a model. In the model, the rate of oxidation of the sample surface was assumed to be expressed as follows:

$$\frac{dq}{dt} = k(q_0 - q), \tag{1}$$

where t, q, q_0 and k are time (s), amount of BeO on the unit surface area (mol/m^2), amount of the final amount of BeO on the unit surface area (mol/m^2) and reaction constant of the unit surface area (s^{-1}), respectively. In the model, the oxide produced on the surface is regarded as BeO. It was also assumed that the reaction constant is expressed as

$$k = k_0 \exp(E_a/RT), \tag{2}$$

where k_0, E_a, R and T are frequency factor (s^{-1}), activation energy (J/mol), gas constant (J/mol K) and absolute temperature (K), respectively. Eq. (1) was numerically solved with the Crank-Nicholson time differential scheme. In computation, the absolute temperature T in Eq. (2) was changed in the way that the temperature of the reactor varied in the experiment as shown in Fig. 2; the variation of temperature measured in the experiment was directly used in computation. Open symbols in Fig. 3 show the change in the total amount of generated H_2, which was calculated from the experimental result shown in Fig. 2. The total amount of hydrogen generated corresponds to the total amount of BeO produced on the surface. The numerical program to solve Eq. (1) was coupled with an algorithm of a least squares analysis, and the values of K_0, E_a and q_0 were simultaneously determined by fitting the result of calculation to the experimental result shown in Fig. 3. The solid line in Fig. 3 shows the best-fit curve obtained in this way. The reactor temperature is shown as the dotted line. The trend of the experimental curve was well reproduced with the rather simple model shown above, which indicates that the model could be appropriate for the expression of the reaction kinetics for oxidation of the surface of titanium beryllide. The values of K_0, E_a and q_0 determined in this way are $1.76 \times 10^6\ s^{-1}$, 240 kJ and 0.133 mol/m^2, respectively. The solid line in Fig. 2

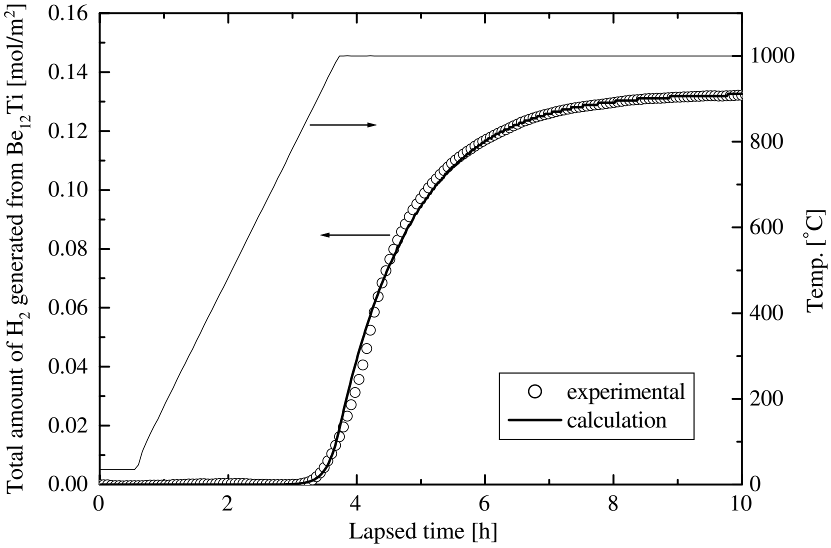

Fig. 3. Change in the total amount of H_2 generated via interaction of H_2O and $Be_{12}Ti$.

shows change in the hydrogen concentration in the outlet stream of the reactor calculated using the numerical program and the values of K_0, E_a and q_0 determined. The experimental result is rather well reproduced by the numerical computation. The result shown above indicates that the reaction kinetics can be expressed as the first order reaction in terms of the unreacted surface area.

Table 1
Positional parameters of $Mn_{12}Th$ and $Be_{12}Mo$

$Mn_{12}Th$ (*I*4/*mmm*)				
Th	2a	$x = 0$	$y = 0$	$z = 0$
Mn-I	8f	$x = 1/4$	$y = 1/4$	$z = 1/4$
Mn-II	8i	$x = 0.361$	$y = 0$	$z = 0$
Mn-III	8j	$x = 0.277$	$y = 1/2$	$z = 0$
$Be_{12}Mo$ (*I*4/*mmm*)				
Mo	2a	$x = 0$	$y = 0$	$z = 0$
Be-I	8f	$x = 1/4$	$y = 1/4$	$z = 1/4$
Be-II	8i	$x = 0.344$	$y = 0$	$z = 0$
Be-III	8j	$x = 0.284$	$y = 1/2$	$z = 0$

5. Ab initio calculation of electron states in $Be_{12}Ti$ crystal

Raeuchle et al. first reported the crystal structure of $Be_{12}Ti$. According to their report, the crystal structure of $Be_{12}Ti$ is the disordered hexagonal with a unit cell $a = 29.44$ Å and $c = 7.33$ Å, but its space group was not clearly specified [7]. After the report, Zalkin et al. redefined the structure of $Be_{12}Ti$ crystal by analyzing their X-ray diffraction data. The reported structure is tetragonal with the unit cell of $a = 7.35$ Å and $c = 4.19$ Å [8]. Then, Gillam et al. have reported that $Be_{12}Ti$ and $Be_{12}V$ have crystal structures similar to that of $Mn_{12}Th$ with the space group of *I*4/*mmm* [9]. However, some positional parameters of beryllium atoms in the crystal structure of $Be_{12}Ti$ as *I*4/*mmm* have not been determined. The crystal structure of $Mn_{12}Th$ defined by Florio et al. is tetragonal (*I*4/*mmm*) with a unit cell $a = 8.74$ Å and $c = 4.95$ Å [10]. The positional parameters of Mn and Th are given in Table 1; the locations are expressed as fractions of Bravais lattice vectors of the unit cell. Raeuchle et al. defined the crystal structure of $Be_{12}Mo$ [11]. According to their report, the crystal structure of $Be_{12}Mo$ is tetragonal with a unit cell $a = 7.271$ Å and $c = 4.234$ Å, and its space group is also *I*4/*mmm*. The positional parameters of Be and Mo are also given in Table 1. In ab initio calculation, the authors used *I*4/*mmm* with the lattice parameters ($a = 7.35$ Å and $c = 4.19$ Å) reported by Zalkin et al. [8]. With regard to the positional parameters of atoms, those reported for $Mn_{12}Th$ and $Be_{12}Mo$ are first tested.

The electron states in the $Be_{12}Ti$ crystal was calculated with CRYSTAL 98 program [12], which can be used for the linear combination of atomic orbital and Hartree-Fock (LCAO-HF) ab initio electron calculation in periodic systems. This code utilizes

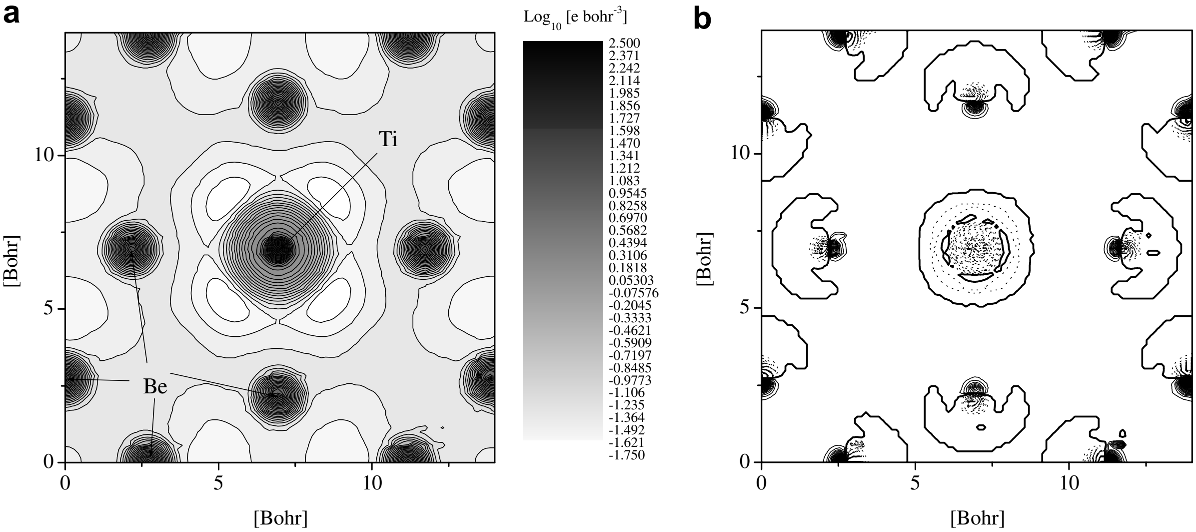

Fig. 4. Electron density map on (0,0,1) plain: (a) electron density map obtained in SCF calculation and (b) electron density difference map.

the linear combination of Bloch function defined in terms of local functions. For the local functions, the Gaussian type functions were used. The Gaussian basis set used for Be was a 5-111G contraction and for Ti a 8-6-411G contraction reported in a literature [13] was used. Convergence in the SCF cycle was controlled by a threshold $\Delta E = 10^{-5}$ hartree per unit cell, and the version of restricted Hartree–Fock (RHF) method was used.

When the positional parameters for $Mn_{12}Th$ was used (the positions of Mn and Th were replaced by Be and Ti, respectively), the converged SCF solution gave the total energy of -1023.29 hartree (-27845.2 eV). In the case of the positional parameters for $Be_{12}Mo$ (the position of Mo was replaced by Ti), the converged SCF solution gave the total energy of -1023.37 hartree (-27847.3 eV). Thus, the positional parameters for $Be_{12}Mo$ resulted in a lower energy state and a more stable structure. Next, the structure optimization was attempted with LoptCG that is a korn-shell script for performing a geometry optimization with CRYSTAL package. The script employs the steepest descent and conjugate gradient approaches. In the structure optimization, the lattice parameters ($a = 7.35$ Å and $c = 4.19$ Å) was held constant, whereas the positional parameters of Be ($x = 0.361$ (Be-II) and $x = 0.277$ (Be-III) for $Be_{12}Mo$) were changed. The crystal structure of $Be_{12}Mo$ was used as the initial structure of $Be_{12}Ti$. The optimized structure gave the total energy of -1023.43 hartree (-27849.0 eV), which is lower than the total energy calculated based on the crystal structure of $Be_{12}Mo$. The positional parameters obtained are $x = 0.3465$ (Be-II) and $x = 0.2994$ (Be-III). The electron density map was generated using these positional parameters. Fig. 4(a) shows the electron density map on the (0,0,1) plane. Contours are increased logarithmically. Electron densities around Be atoms appears to be almost same despite of difference in location. Fig. 4(b) shows the electron density difference map. In this case, contours are increased linearly and the electron density spacing is 0.1 electrons bohr^{-3}. The electron density difference was computed by subtracting the superposition of the electron density of isolated atoms located in the $Be_{12}Ti$ crystal structure from the electron density obtained in the SCF calculation. Continuous and dotted lines indicate positive and negative values, respectively. Thick continuous lines indicate the zero level. Thus, the electron density in the areas expressed with continuous lines increases from the electron density in the isolated state, and that in the area expressed with the dotted lines changes otherwise. The main features observed in Fig. 2(b) are the high electron density difference around Be atom sites and low electron density difference around Ti atom sites. Thus, electrons around the Ti site seem to diffuse or to be extracted by Be atoms located closest to the Ti atom.

6. Conclusions

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 1% at the temperature of as high as 1000 °C. Chaotic breakaway reactions were not observed for the $Be_{12}Ti$ sample, and the amount of hydrogen generated was far smaller in comparison with beryllium. The kinetics of oxidation on the surface of $Be_{12}Ti$ by water vapor was investigated using a model differential equation, and the reaction constant was quantified. Furthermore, to know the electron state in $Be_{12}Ti$, ab initio calculations of quantum chemistry were performed using CRYSTAL 98.

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