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Recent results on beryllium and beryllides in Japan

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Abstract

Recently, several research and development (R&D) programs of beryllium and its alloys for fusion reactor application have been conducted in Japan and the community of beryllium research has grown. In the R&D area of beryllium technology for a solid breeding blanket, a major subject is applications of beryllides, for which lifetime evaluation as neutron multiplier, impurity effect on irradiation behavior and recycling of irradiated materials are under investigation. As for neutron multiplier materials, recent R&D has focused on Be–Ti alloys based on $Be_{12}Ti$ as an advanced option, because of their superior properties compared with beryllium metal in such respects as compatibility with structural materials and oxidation resistance at higher temperatures. In this paper, recent results on beryllide R&D in Japan are described.

1. Introduction

Beryllium metal is one of the most promising candidate materials for the neutron multiplier in the tritium-breeding blanket of fusion reactors [1,2]. However, some problems are anticipated for the use of beryllium in the DEMO blanket where the material encounters high neutron flux and high temperature. The problems anticipated in particular are; beryllium metal will react with the structural material in contact, accumulation of a high tritium inventory, and reaction with water vapor in case of loss-of-coolant accident (LOCA) under such environment [3]. In order to minimize these problems, beryllium based intermetallic compounds have drawn an interest in Japan as an alternative to beryllium metal for neutron multiplier [4].

In previous studies, the beryllium based intermetallic compounds such as $Be_{12}Ti$ and $Be_{12}V$ were selected as candidate materials because of low radio

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activation, high melting point, good oxidation resistance and high beryllium content. Since then, phase equilibria of Be-rich compositions of Be–Ti and Be–V systems were evaluated to optimize the composition and microstructure [5]. Be–Ti alloys have been mainly investigated for easy fabrication by the small scale rotating electrode method (REM) [6]. Preliminary characterizations of Be–Ti alloys have included the compatibility with structural material and ceramic breeder, oxidation, steam reaction, tritium inventory, irradiation effects in JMTR and the structural evolution induced by charged particle irradiation. These preliminary results were summarized in Ref. [7,8]. However, further investigations are necessary both on the fabrication process development and on the characterization of beryllium based intermetallic compounds toward the practical application of the pebbles in a breeding blanket. This paper, describes recent progress on Be–Ti alloys in Japan.

2. Fabrication technology development

$Be_{12}Ti$ pebble productions by REM requires the ingot production by induction melting and vacuum casting to fabricate a appropriate-size electrodes.

Large ingots (200 mm dia × ^{h}400 mm) with two nominal compositions were fabricated and characterized [8]. Actual chemical compositions of the two ingot were Be–8.1 at.%Ti and Be–11.3 at.%Ti. BeO crucibles were used because of a low reactivity with beryllide. Raw materials were beryllium ingots and a Ti block, both of 99.5% purity. Casting mold had an iron chill block on the bottom, so that a large shrinkage formed only on the top of the ingot and a sound portion was obtained near the bottom. The cross section of each ingot was analyzed by X-ray diffraction and optical microscopy to comfirm that Be–8.1 at.%Ti and Be–11.3 at.%Ti are single phase $Be_{12}Ti$ and $Be_{17}Ti_2$, respectively.

It is possible that a further improvement in fabrication of a sound electrode for the REM may involve such a novel casting process as a unidirectional solidification by a floating zone method.

3. Mechanical property of Be–Ti alloys

The temperature dependence of compressive 0.2% flow stress, as expressed by specific strength, of Be–7.7 at.%Ti and Be–9.0 at.%Ti fabricated by arc melting are shown in Fig. 1 together with that of a commercial nickel-base super-alloy IN 738LC [9]. The specific strength at 927°C of Be–8.1at% Ti alloy

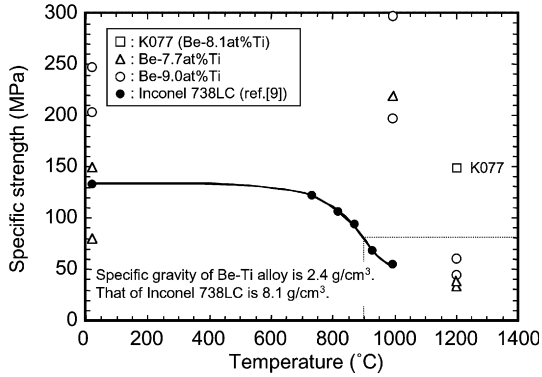

Fig. 1. Relationship between temperature and specific strength of Be–Ti alloys.

(K077) fabricated by the above casting method is shown in the figure. It is obvious that the alloy exhibits the highest strength at the temperature as compared to other Be–Ti alloys and IN738LC. It is noted that the strength of the Be–Ti alloys at room temperature found in Fig. 1 is the fracture stress, which means that the alloys are brittle, exhibiting zero plastic strain at lower temperature. The brittleness is basically an intrinsic property of an alloy consisting mainly of an intermetallic compound.

4. Chemical property of Be–Ti alloys

4.1. Compatibility

The compatibility of Be–Ti alloys (Ti content : 3, 5, 7 and 8.5 at.%) with F82H was evaluated at 600 °C, 700 °C and 800 °C for times up to 1000 h. For Be–Ti alloys and F82H, reaction and diffusion layers were observed on the F82H side after exposures. The thickness of the reaction layer was smaller than between Be and F82H after exposure at 700 and 800 °C. Fig. 2 shows results of thickness measurements of the reaction layer. The thickness of the reaction layer between Be–Ti alloys and F82H after annealing at 600 °C for 1000 h was less than 3 μm, whereas the reaction layer with beryllium metal was about 15 μm. At 800 °C for 1000 h, the thickness of the reaction layer of Be–5 at.%Ti and Be–7 at.%Ti was less than 50 μm. It is obvious that the compatibility of Be–Ti alloy with F82H was much better than that between Be and F82H [10].

4.2. Oxidation resistance

As reported earlier, oxidation resistance of Ti-beryllides is very good at 800 °C in dry air [11]. In

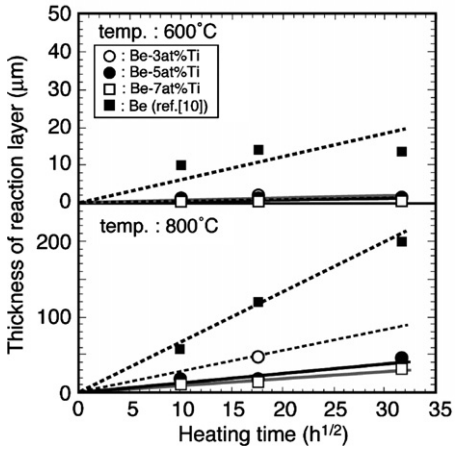

Fig. 2. Change in thickness of the reaction layer with annealing time (Compatibility between Be–Ti alloys and F82H steel).

this work, the oxidation behavior of Ti-beryllides, which contain intermetallic compound phases $Be_{12}Ti$ (7.7 at.%Ti), $Be_{10}Ti$ (9.0 at.%Ti) and $Be_{17}Ti_2$ (10.5 at.%Ti) was investigated at higher temperatures. Fig. 3 shows the mass gain curves of Be and three kinds of Ti-beryllides at 1000 °C in dry air. All the mass gain curves for beryllides were nearly flat, in contrast to Be which has large mass gain. And there seems to be little difference in mass gain among the three Ti-beryllides.

From this result, the oxidation resistance of Ti-beryllides is believed to be good enough for application even at a temperature of 1000 °C.

4.3. Surface analysis

Surface analyses by X-ray photoelectron spectroscopy (XPS) was carried out for Be–7 at.%Ti disk before and after heating for 10 min in vacuum (1×10^{-7} Pa) at temperatures from 200 to 800 °C.

Before heating, the surface composition was C: 45.8 at.%, O: 32.7 at.%, Be: 21.0 at.%, and Ti: 0.5 at.%. The concentration ratio of Ti to Be, [Ti]/[Be], was 0.024 and significantly smaller than that in the bulk (0.075). A major portion of Be was present as BeO as shown in Fig. 4(a), and the rest of Be was in a metallic state. Ti existed mainly in a metallic state and as TiO_2 (see Fig. 4(b)). A significant change in the surface state was observed above 300 °C. A major portion of Be was in the state of BeO even at 800 °C. In the case of the pure Be specimen examined in the previous study [12], a major part of Be was converted from BeO to metallic Be at this temperature. This difference indicates that the transport of Be through the oxide layer was retarded by alloying with Ti.

4.4. Steam interaction

The chemical stability of $Be_{12}Ti$ was investigated in a stream of argon gas containing 1% water vapor

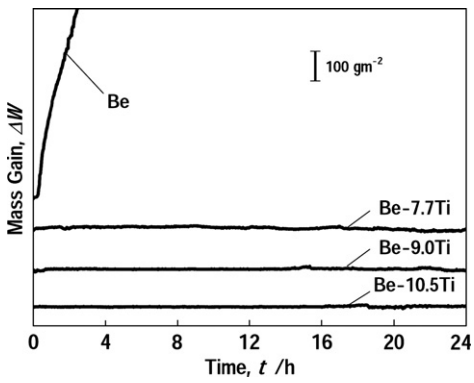

Fig. 3. Mass gain curves of Be–7.7 at.%Ti, Be–9.0 at.%Ti and Be–10.5 at.%Ti at 1000 °C in dry air.

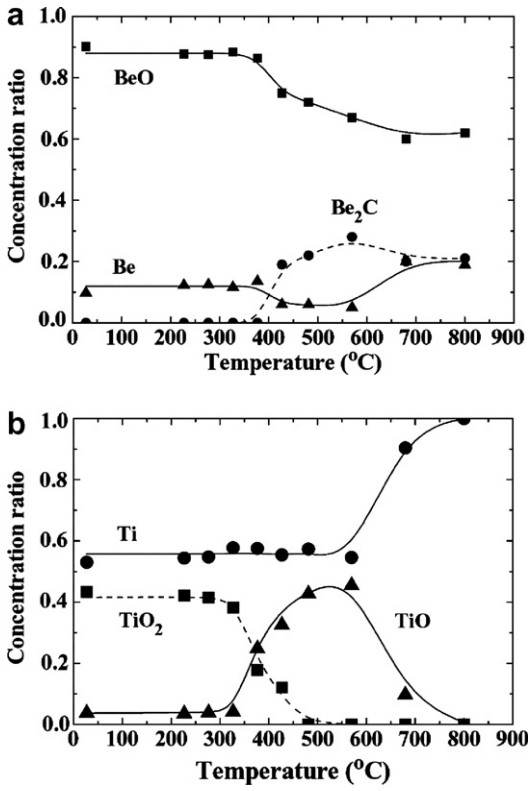

Fig. 4. Changes in chemical states of Be (a) and Ti (b) by heating in vacuum.

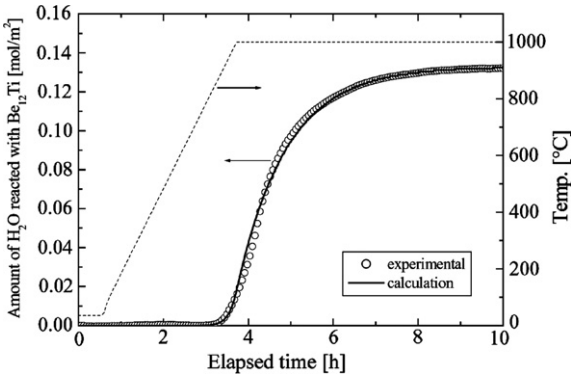

Fig. 5. Change in total amount of H_2O reacted with $Be_{12}Ti$.

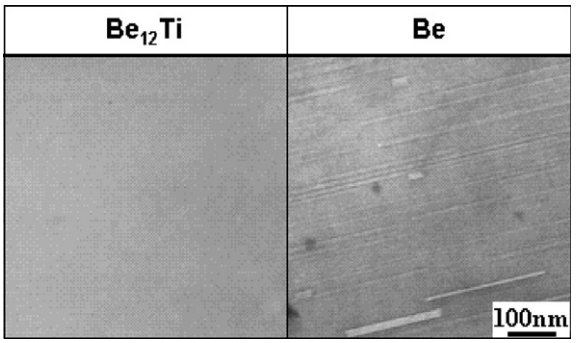

Fig. 6. Transmission-electron micrograph of $Be_{12}Ti$ and beryllium irradiated with 8 keV-D_2^+ to dose of 2×10^{21} D^+/m^2 at 400 °C.

[13]. Open symbols in Fig. 5 show the total amount of H_2O reacted with $Be_{12}Ti$. The broken line shows the reactor temperature. The generation of hydrogen started at a temperature near 800°C, and terminated 10 h later. No breakaway reaction was observed. The amount of oxidized $Be_{12}Ti$ is far smaller than in similar conditions with beryllium.

The numerical program to solve equation [13] was coupled with an algorithm of a least squares analysis, and the values of frequency factor (k_0), activation energy (E_a) and amount of the final amount of BeO on the unit surface area (q_0) were determined by fitting the calculated curve to the experimental result. The solid line in Fig. 5 shows the best-fit curve obtained. The values of k_0, E_a and q_0 determined are 1.76×10^6 s^{-1}, 240 kJ and 0.133 mol/m^2, respectively. The result shown above suggests that the reaction kinetics can be expressed as the first order reaction in terms of the unreacted surface area.

5. Irradiation effects in Be–Ti alloys

5.1. Tritium inventory

Thermal desorption of deuterium from $Be_{12}Ti$ irradiated by D_2^+ ions and microstructural change during irradiation were examined to understand deuterium retention and desorption properties.

Fig. 6 shows transmission-electron micrographs of $Be_{12}Ti$ and beryllium irradiated with 8 keV-D_2^+ at 400 °C to dose of 2×10^{21} D^+/m^2. A large number of linear defects a single direction were observed in beryllium, and it was established that this defect was a three-dimensional cavity [14]. Some authors suggest that these cavities in the beryllium accommodate the deuterium as D_2 molecules [14,15]. Therefore, the long, slender cavities are responsible for high retention of deuterium in this case. In the $Be_{12}Ti$, on the other hand, no defect was observed for this irradiation condition. This fact indicates that nucleation of cavities is not easy in this irradiation condition. Deuterium trapping sites in the $Be_{12}Ti$ are believed to be very small vacancy clusters (<2 nm) and impurities.

In conclusion, it seems reasonable to expect low swelling and low hydrogen isotope retention under neutron irradiation at temperature around 400 °C.

5.2. Charged particle irradiation

The synergistic effects of helium transmutation and irradiation damage on microstructural evolution in pure Be and $Be_{12}Ti$ have been studied by in-situ observation using the Multi Beam High Voltage Electron Microscope (MB-HVEM) in Hokkaido University, Japan. After electron-He ion dual beam irradiation to 2.15×10^{22} e/cm^2 with 1.40×10^{15}He ions/cm^2 at RT, many bubbles were observed in pure Be, but less bubble formation was observed in $Be_{12}Ti$. As increasing irradiation temperature to 500 °C at the same irradiation dose, still less bubble formation was observed in $Be_{12}Ti$. However, some tiny bubbles were observed along the sub grain boundary in $Be_{12}Ti$ (see Fig. 7), and it was hard to observe black dots or dislocation loops associated with radiation induced interstitials in $Be_{12}Ti$ under other diffraction condition. This result suggested that interstitial may be immobile due to its complex crystallographic structure in this experimental condition.

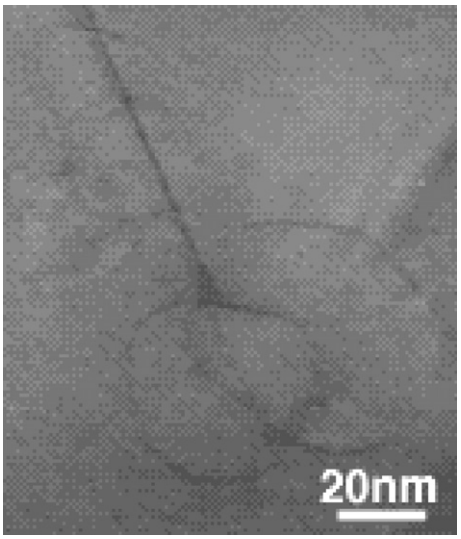

Fig. 7. TEM micrographs of $Be_{12}Ti$ at 500 °C after electron-He ion dual beam irradiation. (2.15×10^{22} e/cm^2–1.40×10^{15}He ions/cm^2).

5.3. Neutron irradiation

It is necessary to have high neutron dose irradiation tests to evaluate lifetime. In the frame of an IEA collaborative program between Japan and Europe, irradiation tests of Be–Ti alloys (Be–5 at.%Ti and Be–7 at.%Ti) were started in 2005 in the HFR reactor in Petten (NL) [16].

6. Conclusion

The basic physical, chemical and mechanical properties of stoichiometric $Be_{12}Ti$ fabricated by HIP, and Be–Ti alloy with α-Be phase fabricated by an arc melting process have been studied and have shown some advantages over beryllium. For the compatibility between Be–Ti alloys and F82H, the growth rate of the reaction layer for the Be–Ti alloys decreased with increasing the Ti content in the Be–Ti alloy. Oxidation resistance, tritium inventory and irradiation effects of Be–Ti alloys have been evaluated and these properties of Be–Ti alloys were better than those of Beryllium. Further experiments on Be–Ti alloys will include irradiations using various accelerators and test reactors to high dose to clarify the advantages of the Be–Ti materials.

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