Synthesis of Be–Ti–V ternary beryllium intermetallic compounds

Jae-Hwan Kim *, Masaru Nakamichi

Breeding Functional Materials Development Group, Department of Blanket Systems Research, Rokkasho Fusion Institute, Sector of Fusion Research and Development, Japan Atomic Energy Agency, Japan

A B S T R A C T

Beryllium intermetallic compounds (beryllides) such as $Be_{12}Ti$ and $Be_{12}V$ are the most promising advanced neutron multipliers in demonstration power reactors. Advanced neutron multipliers are being developed by Japan and the EU as part of their Broader Approach activities. It has been previously shown, however, that beryllides are too brittle to fabricate into pebble- or rod-like shapes using conventional methods such as arc melting and hot isostatic pressing. To overcome this issue, we developed a new combined plasma sintering and rotating electrode method for the fabrication of beryllide rods and pebbles.

Previously, we prepared a beryllide pebble with a Be–7.7 at.% Ti composition as the stoichiometric value of the $Be_{12}Ti$ phase; however, $Be_{17}Ti_2$ and Be phases were present along with the $Be_{12}Ti$ phase that formed as the result of a peritectic reaction due to re-melting during granulation using the rotating electrode method. This Be phase was found to be highly reactive with oxygen and water vapor. Accordingly, to investigate the Be phase reduction and applicability for fabrication of electrodes prior to granulation using the rotating electrode method, Be–Ti–V ternary beryllides were synthesized using the plasma sintering method.

Surface observation results indicated that increasing plasma sintering time and V addition led to an increase in the intermetallic compound phases compared with plasma-sintered beryllide with a Be–7.7 at.% Ti composition. Additionally, evaluation of the reactivity of samples with water vapor at high temperature revealed that specimens with larger fractions of Be phases experienced larger weight gains and H_2 generation rates because of oxidation, as $Be_{12}Ti$ and $Be_{12}V$ phases have a similar oxidation tendency.

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1. Introduction

Beryllium intermetallic compounds (beryllides) such as $Be_{12}Ti$ and $Be_{12}V$ are the most promising advanced neutron multipliers for solid breeder water cooling blankets in demonstration (DEMO) power reactors. Advanced neutron multipliers are being developed by Japan and the EU as part of their Broader Approach activities. It has been previously shown, however, that beryllides are too brittle to be fabricated in pebble- or rod-like shapes using conventional methods such as arc melting [1] and hot isostatic pressing [2]. We have developed a plasma sintering method that results in surface activation of the starting powder particles, enhancing their sinterability and reducing high temperature exposure. This method has been applied to the preliminary synthesis of beryllide by Nakamichi et al. [3] as a nonconventional consolidation process consisting of plasma generation, resistance heating, and pressure application. Beryllide was successfully synthesized,

although a longer sintering time of more than 90 min was necessary for homogenization to a single $Be_{12}Ti$ phase.

Furthermore, we previously investigated the effect of sintering conditions on the sinterability [4] and optimization [5] of Be–7.7 at.% Ti intermetallic compounds, which are stoichiometric to $Be_{12}Ti$. Additionally, Be–X at.% Ti (X = 3–10.5) was also studied to further investigate the fabrication and mechanical properties of beryllide block compounds [6] and the granulation and stability of beryllide pebbles at high temperature [7]. Most of these materials have been associated with binary Ti beryllides, because Ti is superior based on its threshold energy and neutron absorption cross section. However, Ochiai et al. [8] demonstrated using a simple calculation that V exhibits nuclear properties similar to those of Ti in binary beryllides. Beryllide pebbles with 7.7 at.% Ti were found to require additional homogenization to achieve pebbles with a single $Be_{12}Ti$ phase [9]. Therefore, not only Be–V binary beryllides but also Be–Ti–V ternary beryllides should be further investigated.

In addition to this fusion application, both beryllium and lithium targets have been used as a target material for neutron

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* Corresponding author. Tel.: +81 175 71 6537; fax: +81 175 71 6502.
  E-mail address: kim.jaehwan@jaea.go.jp (J.-H. Kim).

production in accelerator-based boron neutron capture therapy (BNCT) [10]. The beryllium target has been broadly applied from viewpoint of cooling efficiency by water. Because of reactivity between the target and water vapor, however, a development of advanced target materials is inevitable. Since the beryllide has indicated much higher stability than beryllium metals [11], it can be substituted for the target material in the accelerator-based BNCT.

Herein we report the synthesis of Be–Ti–V ternary beryllides prepared using the plasma sintering method prior to fabrication of ternary beryllide pebbles and the effect of the phase composition on their reactivity behavior.

2. Material and methods

The Be–Ti–V ternary beryllides were synthesized using a plasma sintering method [4,5]. Be, Ti, and V powders with purities of 99.5%, 99.9%, and 99.0% and particle sizes less than 45, 45, and 75 μm, respectively, were used. The powders were mixed with compositions $Be_{12}Ti_{0.9}V_{0.1}$, $Be_{12}Ti_{0.7}V_{0.3}$, $Be_{12}Ti_{0.5}V_{0.5}$, $Be_{12}Ti_{0.3}V_{0.7}$, and $Be_{12}Ti_{0.1}V_{0.9}$ using a mortar (RM200, Retsch, Germany) for 1 h and then loaded into a graphite punch and die for cold compaction. Prior to sintering, an alternate current of 200 A was applied for 30 s to each powder to activate the powder surfaces and remove any impurities. Sintering was conducted at 1273 K for 20 min using heating and cooling rates of 100 and 200 K/min, respectively.

The intermetallic phases of the beryllides were observed using an electron probe micro-analyzer (JXA-8530F, JEOL, Japan) with backscattered electrons and point analysis of each phase by wavelength dispersive X-ray spectrometer. To confirm the composition of each phase, X-ray diffraction analysis (XRD, UltimaIV, Rigaku, Japan) was performed. To estimate the sinterability of the ternary beryllides, their densities were determined using the He pycnometer and water immersion methods. Furthermore, to evaluate their stability at high temperature, the weight gain and H_2 generation behavior of the beryllides with different compositions were measured at 1073, 1273, and 1473 K for 24 h in 1% H_2O/Ar atmosphere using thermal gravimetry and gas chromatography, respectively. Finally, after completion of the reactivity tests at high temperature, the phase stability of the beryllides was investigated by determining the phase variation using scanning electron microscopy (SEM)/electron probe micro-analyzer (EPMA).

3. Results and discussion

Few phase diagrams have been developed for ternary Be–Ti–V beryllides, although phase diagrams for binary Be–Ti and Be–V [12] have been previously reported. Fig. 1 presents the ternary phase diagram for Be–Ti–V at 1273 K based on theoretical calculations [13]. The isothermal section at 1273 K indicates that $Be_{12}Ti$ and $Be_{12}V$ form a continuous, isomorphous solid solution, because the crystal structures of these two compounds are the same [13].

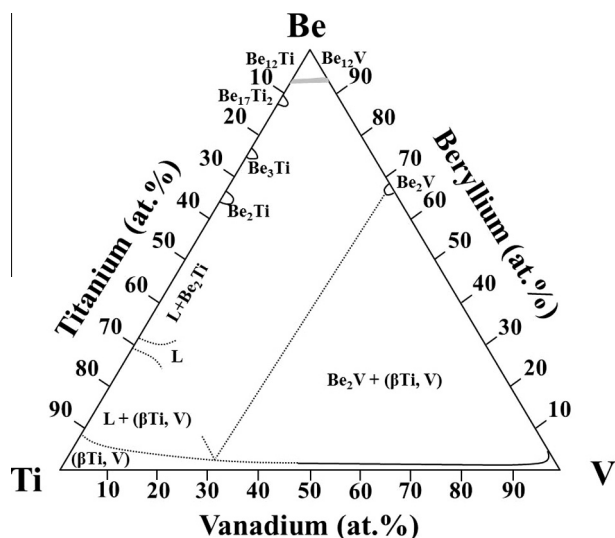**Fig. 1.** Ternary phase diagram of beryllide at 1273 K based on theoretical calculations [13].

The phase diagram also reveals that $Be_{12}Ti$ and $Be_{12}V$ (gray area) exist in ternary $Be_{12}Ti_{1-x}V_x$ ($x = 0.1$, 0.3, 0.5, 0.7 and 0.9). However, few studies on the phase compositions of plasma-sintered beryllides have been reported. Previously [5], it was clarified that binary Be–Ti beryllides consist of four different phases (Be, $Be_{12}Ti$, $Be_{17}Ti_2$, and Be_2Ti,) because the sintering temperature and time were not sufficient for homogenization. This result suggested that higher sintering temperatures and longer sintering times provide beryllides with higher fractions of the $Be_{12}Ti$ phase. In the present study, the phase compositions of the beryllides were investigated as a function of the amount of added V.

Fig. 2 presents SEM images of the beryllides plasma-sintered at 1273 K for 20 min. Two gray phases with slightly different contrasts can be clearly seen in Fig. 2(a) and (b), indicating that with an increase in x in $Be_{12}Ti_{1-x}V_x$, the area fractions of the Be and $Be_{12}V$ phases increased, whereas that of the $Be_{12}Ti$ phase decreased. It was very difficult, however, to separate these areas into the $Be_{12}Ti$ and $Be_{12}V$ phases on the basis of contrast differences observed in the SEM images obtained using backscattered electrons to evaluate their individual fractions, because there is no significant difference in the atomic numbers of Ti and V. On the other hand, it can be seen in the SEM images of the beryllides that the fraction of the gray-colored phase with a slightly lighter gray contrast (white arrow) increased as the V content increased.

Fig. 3 shows the area fractions of each phase in the ternary beryllides with different compositions. The area fractions for both $Be_{17}Ti_2$ and Be_2V and both Be_2Ti and V, which seemed to be similar in color, were nearly the same, whereas those for both $Be_{12}Ti$ and $Be_{12}V$ and Be in the beryllides exhibited evident tendencies to decrease and increase, respectively. Furthermore, the X-ray diffraction results (Fig. 4) were in good agreement with the area fractions and SEM observations; the peak intensities for $Be_{12}V$ (42.9° and 50.0°) increased, while those for $Be_{12}Ti$ (42.5° and 49.5°) decreased as the amount of added V increased. Because the melting point of the starting powder increased as V content in the beryllides increased, it is thought that under identical sintering temperature, the powders did not consolidate to targeting composition remaining larger fraction of Be phase due to this increase of the melting point.

The sinterability of the beryllides plasma-sintered at 1273 K for 20 min was assessed by evaluating their densities, which were determined using both the He gas pycnometer and water immersion methods. The porosities were then calculated by subtracting the density values obtained using the He pycnometer from those obtained using the water immersion method.

Fig. 5 shows the densities of the beryllides as a function of the V content. It can be observed that, as the amount of added V increased, the densities increased because of the higher density of V. Moreover, the porosity clearly increased with increasing V addition. This result may have occurred not because the starting V powder particle size was approximately twice that of the Be and Ti powders (less than 75 μm vs. less than 45 μm, respectively), but because the melting temperature increased as the amount of added V increased. In fact, differences in powder sizes typically result in a decrease in the porosity as the V content increases; therefore, the increase in porosity was likely caused by the differences in the melting temperatures at the same sintering temperature and time.

For advanced multipliers as well as neutron target in the accelerator-based BNCT, high temperature reactivity is the most important property because the materials are exposed to high temperatures and severe atmosphere, particularly when a loss of coolant accident (LOCA) occurs and cooling condition, respectively. Therefore, the weight gains of the beryllides were evaluated in 1% H_2O/Ar atmosphere at different temperatures (1073, 1273, and 1473 K) for 24 h, and the results are shown in Fig. 6. It can be seen