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Optimization of synthesis conditions for plasma-sintered beryllium–titanium intermetallic compounds

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ABSTRACT

Plasma sintering method has been newly suggested as a synthesis method for beryllium–titanium intermetallic compounds (beryllides) as an advanced neutron multiplier in a system of water cooled solid breeder demonstration fusion reactors. Not only synthesis of the beryllide but joining the beryllide could be successfully fabricated. We report on the optimization of the main sintering conditions, on the sinterability of the plasma-sintered beryllides in the light of sinterability, as well as consolidation to the $Be_{12}Ti$ phase. The optimum sintering temperature for consolidation to the $Be_{12}Ti$ phase was 1273 K and the area fraction of the $Be_{12}Ti$ phase obtained when sintering at 1273 K, was approximately 83%. To increase the fraction of the $Be_{12}Ti$ phase, increasing the sintering time was inevitable and this led to an increase in the $Be_{12}Ti$ phase corresponding to 97.5%. However, as the sintering time increased, variation in grain size of the beryllides was observed. With regard to the sintering pressure, the higher the sintering pressure applied, the higher the sinterability, even though lower pressure may lead to better consolidation with respect to the absence of the Be_2Ti phase.

1. Introduction

Beryllides (beryllium intermetallic compounds) have been known as advanced neutron multipliers which are loaded as a pebble bed type in fusion demonstration reactors. However, beryllide fabrication of either the rod- or pebble-type is regarded to be considerably difficult owing to the material's brittleness. Despite this shortcoming, many methods such as, hot isostatic pressing (HIP) [1], vacuum casting [2,3], and the arc melting method [4–6] have been performed for beryllide synthesis. With the success of the synthesis, several disadvantages have arisen, such as complicated processes involving repeating cold and hot isostatic pressings and long time-consuming processes for homogenization to the target composition. Nakamichi et al. have suggested the plasma sintering method for beryllide synthesis and have demonstrated that the beryllide was successfully synthesized [7] and joined for the fabrication of the beryllide rod [8] prior to the rotating electrode method and that using the rod led to successful fabrication of beryllide pebbles [9]. Despite this being one of the sintering processes, few studies have been found on the sintering conditions for the plasma-sintered beryllide. These studies on the advanced neutron multipliers are being developed by supports of the International Fusion Energy Research Centre (IFERC) project as part of the Broader Approach (BA) activities between 2007 and 2016.

In this study, several sintering conditions for the beryllide, such as sintering temperature, time, pressure and heating/cooling rate are reported from the viewpoint of not only consolidation to $Be_{12}Ti$ but sinterability.

2. Materials and methods

Starting powders used in this study were Be and Ti powder (<45 μm, Materion, USA). The starting powders were mixed with a stoichiometric composition of $Be_{12}Ti$ by means of mortar (RM200, Retsch, Germany) for 60 min. The powder was loaded into a graphite punch and die unit with the application of uniaxial pressure for cold compaction. An on–off electric direct current with approximately 500 A for 30 s was applied to create the plasma environment and thus activate the particle surfaces to get rid of impurities on the surface of the loaded powder. The powder compact was resistance-heated while uniaxial pressure was applied to the material. To investigate the effects of the sintering conditions on the sinterability, sintering temperature, sintering time and sintering pressure were varied. Because these are well-known to be the important variables for the sintering process, it is necessary to investigate the effect of the variables on the sinterability as well as on consolidation to $Be_{12}Ti$. With the exception of the sintering temperature, time, and pressure, the other conditions were fixed for greater clarity. Herein, the sintering temperatures are 973, 1073, 1173, 1273 and 1373 K while the time and pressure are fixed to 20 min and 50 MPa, respectively. To investigate the effect of sintering times on sinterability, the times were varied as 5, 10, 30, 60 and 90 min and the temperature and pressure to 1273 K and 50 MPa, respectively. For both experiments, sintering pressures were 50 MPa which is available for conventional maximum graphite punch and die unit used in this study. In addition, we investigated the effect of the sintering pressure on the sinterability of beryllide, varying the sintering pres-

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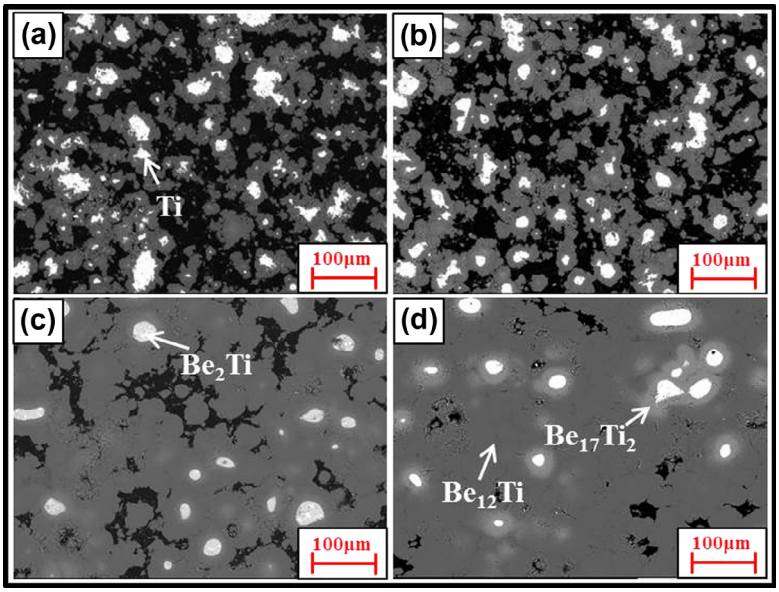

Fig. 1. SEM images of the beryllide sintered at (a) 973, (b) 1073, (c) 1173 and (d) 1273 K.

sures to 17, 25, 33, 42, and 50 MPa while the temperature and time were fixed at 1273 K and 20 min, respectively. For all fabrication conditions, heating and cooling rates were fixed at 100 K/min and 200 K/min, respectively. Finally, to investigate the effect of the heating and cooling rate on synthesis of $Be_{12}Ti$, heating and cooling rate were varied as 10, 50, 100 and 200 K/min while the sintering temperature, time and pressure were fixed to 1273 K, 10 min and 50 MPa, respectively. After plasma sintering under the above conditions, all samples were cut to $3 \times 3 \times 5$ μm using a wire electrical discharge machine (FANUC, Japan) and polished up to 15 μm. For the relative density of the plasma-sintered beryllides, a gas pycnometer (AccupycII 1340-1CC, Shimadzu, Japan) was used. The relative density was calculated by comparing the measured density and theoretical density, calculated by area fractions for each phase. For evaluation of the qualitative analysis, the electron probe microanalyzer (JXA-8530F, JEOL, Japan), with scanning electron microscopic observation using back-scattered electrons, as well as phase composition analysis, was used. To support the analysis of the phase composition precisely, X-ray diffraction measurement (UltimaIV, Rigaku, Japan) was undertaken with scan speeds of 0.01° from 10° to 100° to confirm the compositional variation of beryllides with different Ti amounts. We additionally report on the micro-Vickers hardness results (HM-221, Mitsutoyo, Japan) and grain size variation according to different sintering conditions. Evaluation of the grain size of the beryllides was carried out using an optical microscope (VK 9700, KEYENCE, Japan) after chemical etching, which blended H_2O, HNO_3, and HF.

3. Results and discussion

3.1. Sintering temperature

In the sintering process, selection of the sintering temperature is the most important factor because it is closely associated with consolidation of the target composition, herein, the $Be_{12}Ti$ phase. In general, a higher temperature accelerates volume diffusion compared to interfacial diffusion. Accordingly, a densification mechanism may dominantly change with temperature. The temperature should be decided at a certain range because insufficient consolidation of the target composition and breaking due to unexpected reaction may take place.

In this study, the sintering temperatures were varied to 973 K, 1073 K, 1173 K, 1273 K, and 1373 K to investigate the sintering temperature dependence of the consolidation to $Be_{12}Ti$ in the plasma-sintered beryllides. Under several trials for reproducibility, plasma-sintered beryllides were fabricated. The beryllides sintered at 1373 K, however, were broken despite several tries. From the observation of the sample, the breaking seems to be due to the reaction between the beryllium and the carbon from the graphite punch and die unit. On the other hand, the beryllides sintered at 973 K, 1073 K, 1173 K, and 1273 K were successfully fabricated.

Fig. 1 shows the back-scattered electron scanning electron microimages of the samples fabricated by the plasma-sintered method, demonstrating that the beryllides are composed of four different phases, Be, $Be_{12}Ti$, $Be_{17}Ti_2$, and Be_2Ti (or Ti in the cases of 973 K and 1073 K) corresponding to black, gray, light gray, and white areas, respectively. However, for the beryllides sintered at 973 K and 1073 K, a small amount of Ti was identified while no Ti was found when sintered at both 1173 K and 1273 K. Since the plasma sintering process leads to heat variation among the powders, it is considered that the existence of Ti may be caused by insufficient temperature with which to consolidate. The area fractions of each phase are given in Fig. 2, clarifying that increasing the sintering temperature, increases the $Be_{12}Ti$ phase while decreasing the Be and Be_2Ti phases. The $Be_{17}Ti_2$ phase started to form in the beryllides sintered at above 1073 K, albeit negligibly. The increase

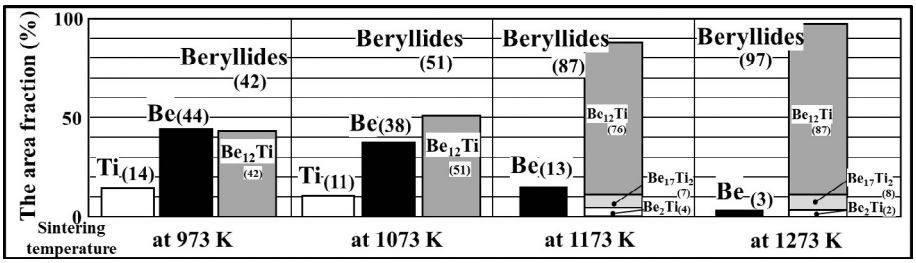

Fig. 2. Area fractions of each phase sintered at 973, 1073, 1173 and 1273 K for 20 min.