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Comparative study of sinterability and thermal stability in plasma-sintered niobium and vanadium beryllides

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ABSTRACT

Niobium and vanadium–beryllium intermetallic compounds (beryllides) were synthesized by plasma sintering under different sintering times at 1273 K. The beryllide with 7.7 at.% Nb mainly consisted of various phases of Be, $Be_{12}Nb$, $Be_{17}Nb_2$, and Be_2Nb, whereas that with 7.7 at.% V consisted of $Be_{12}V$, Be_2V, and V. As the sintering time increased, area fractions of the target compositions $Be_{12}Nb$ and $Be_{12}V$ increased while that of Be decreased. A comparative analysis demonstrated that the beryllide with 7.7 at.% Nb a showed higher density as well as a greater hardness than that with 7.7 at.% V, due to there being less difference between the sintering temperature and the melting point. In terms of thermal phase stability, the beryllide with 7.7 at.% Nb showed good thermal phase stability with fewer pores and a smaller unhomogenized area, because the beryllide contained a smaller area fraction of the Be phase, which may cause evaporation resulting in pore formation.

1. Introduction

Beryllium intermetallic compounds (beryllides) have attracted a great deal of attention as refractory materials and advanced neutron multipliers for use in the demonstration (DEMO) fusion reactor, owing to their high stability at high temperature. However, there is no doubt that the beryllides are too brittle to be fabricated in small size. As a part of the Broader Approach activities from 2007 to 2016 on DEMO R&D for the International Fusion Energy Research Centre (IFERC) project, our group has reported that the binary beryllium and titanium intermetallic compounds were easily and successfully synthesized by a plasma-sintering method [1–5]. In previous research on preliminary synthesis of V and Nb beryllides [6], X-ray diffraction analysis clearly depicted the syntheses of $Be_{12}V$ and $Be_{12}Nb$ compounds. Furthermore, beryllides have been reported for use as neutron multipliers in both form of a disk [7] and form of pebbles [8] with a diameter of 1 mm, in light of their mechanical properties and microstructural variation.

In addition, new functional materials for use in the fusion field may be considered in addition to the already-existing ones, owing to high temperature stability. Bruemmer et al. [9] reported that hot isostatically-pressed $Be_{12}Nb$ and $Be_{17}Nb_2$ indicated reasonable strength at both high and low temperature as refractory material application. Furthermore, study on the superconducting property of $BeNb_3$ has been reported with a structural evaluation by Tuleushev et al. [10]. With regards to Be–V intermetallic compounds, Kurinskiy et al. [11] reported that $Be_{12}V$ intermetallic compounds indicated similar brittle behavior to that which caused the failure of $Be_{12}Ti$ as a neutron-multiplying material.

In the present study, $Be_{12}Nb$ and $Be_{12}V$ were synthesized by the plasma-sintering method with different sintering times to investigate their sinterability and thermal stability. In addition, to evaluate the thermal stability, an annealing test at 1473 K was carried out with $Be_{12}Nb$ and $Be_{12}V$, and the result was explained with structural evolution.

2. Materials and method

The binary beryllides were synthesized by the plasma-sintering method [5]. Beryllium, niobium, and vanadium powders with high purities of 99.5%, 99.9%, and 99.0%, and particle sizes of less than 45, 45, and 75 μm, respectively, were used. As shown in Fig. 1, the powders were mixed at concentrations of 92.3 at.% Be, 7.7 at.% Nb or V to produce $Be_{12}Nb$ and $Be_{12}V$ using a mortar (RM200, Retsch, Germany) for 1 h and then loading into a graphite punch and die for cold compact. Prior to sintering, an alternating current of 500 A was applied for 30 s to activate the powder surface. The sintering was conducted at 1273 K for holding times of 5 min, 20 min, and 60 min with heating and cooling rates of 100 K/min and 200 K/min, respectively.

For characterization, the beryllides were cut into 3 × 3 × 5 mm samples and polished up to 15 μm with SiC sand paper. To investigate the sintering density of the beryllide including open porosity, the Archimedes immersion method and a He gas pycno-meter (AccupycII 1340-1CC, Shimadzu, Japan) were used. Sintering

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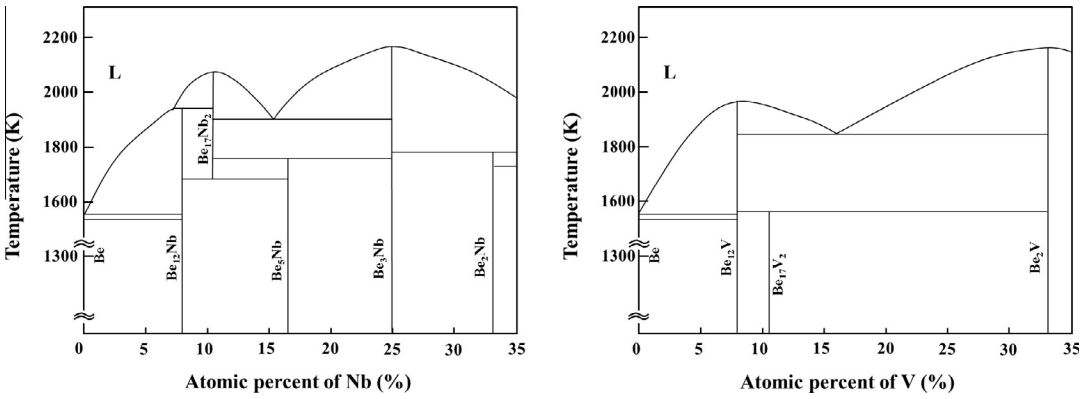

Fig. 1. Phase diagrams of Be–Nb (left) and Be–V (right).

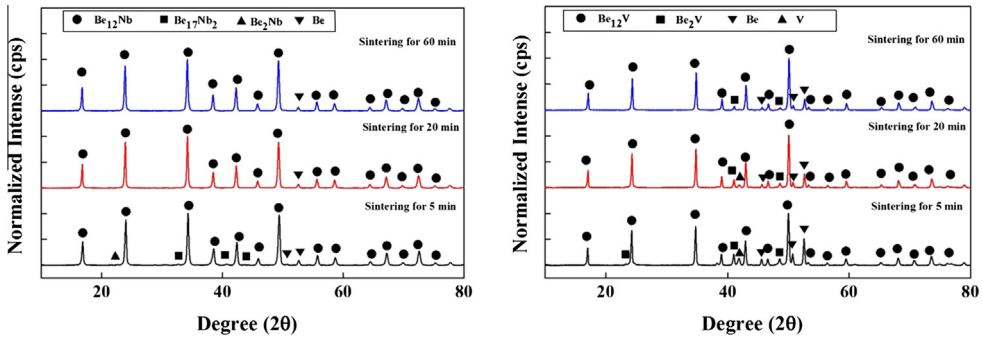

Fig. 2. X-ray diffraction profiles of the beryllides sintered for 5, 20, and 60 min.

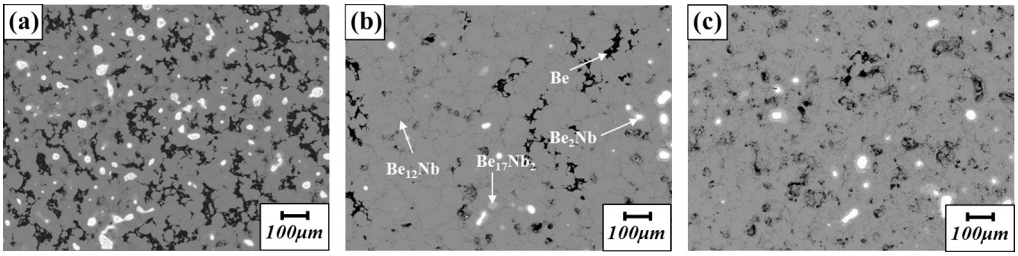

Fig. 3. SEM images of the niobium beryllides plasma-sintered at 1273 K for (a) 5 min, (b) 20 min, and (c) 60 min.

density was calculated by theoretical density based on the area fraction of each phase, and the apparent density measured by the immersion method with open porosity was evaluated by densities measured by immersion and He pycno-meter methods.

The intermetallic phases of the beryllides were observed using an electron probe micro-analyzer (EPMA, JXA-8530F, JEOL, Japan) with electron back-scatter for the point analysis of each phase. To confirm the composition of the each phase, X-ray diffraction analysis (UltimaIV, Rigaku, Japan) and point analysis were carried out by the EPMA. The area fractions of each phase in the beryllides, were calculated by an image-analyzing program (ImageJ 1.44p, National Institutes of Health, USA). To evaluate the mechanical properties, the Vickers micro-hardness (HM-221, Mitsutoyo, Japan) was measured at 16 points with a pressure of 1 kg_f/mm^2. In addition, the samples were heated to 1473 K for 5 h (KEF-1600, Kaken, Japan) and observed by the EPMA to investigate the thermal stability of the beryllides.

3. Results and discussion

To identify the phases in each beryllide sample, X-ray diffraction measurements were performed. Fig. 2 shows X-ray diffraction results for Be–7.7 at.% Nb (left) and Be–7.7 at.% V (right). The qualitative X-ray diffraction results implied that the Be–Nb beryllide samples consisted of four phases, $Be_{12}Nb$, $Be_{17}Nb_2$, Be_2Nb, and Be, in a sample sintered for 5 min, and that as the sintering time increased, $Be_{17}Nb_2$, Be_2Nb, and Be decreased whereas $Be_{12}Nb$ increased. Conversely, with regards to Be–V beryllide samples, X-ray diffraction profiles confirmed the identification of four phases, $Be_{12}V$, Be_2V, Be, and V, implying that with increasing sintering time, Be_2V, Be, and V peaks have a tendency to decrease while $Be_{12}V$ peaks relatively increase. This identification is in good agreement with phase diagrams (see Fig. 1).

For quantitative evaluation of each phase, surface observation and image analysis were conducted. SEM images of the beryllides synthesized from Be–7.7 at.% Nb by plasma sintering are shown in Fig. 3, which shows that the beryllide samples consisted of four different contrasting hues: black, gray, light gray, and white, which corresponded to Be, $Be_{12}Nb$, $Be_{17}Nb_2$, and Be_2Nb, respectively (see (b)). In the case of beryllide sintered for 5 min, larger fractions of the Be and Be_2Nb phases were detected, while the $Be_{12}Nb$ phase, which is target composition, was successfully synthesized. With regards to phase evolution according to sintering time, it was obvious that, with increased sintering time, the area fraction of the $Be_{12}Nb$ phase increased. The area fractions calculated by image