

Mechanochemically assisted preparation of NbB₂ powder

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Abstract

A powder mixture of Nb-B (1:2) was milled using milling media of different sizes in a planetary ball mill, and NbB₂ was mechanochemically prepared. When the mixture was milled with 5 mm diameter balls, NbB₂ started to form in 20 h and the single phase NbB₂ was obtained in 50 h. The time required for the NbB₂ formation and the single phase decreased with the increase in the ball size. The lattice parameters of the NbB₂ obtained were $a = 0.3112$ nm, $c = 0.3276$ nm. The average particle size of the NbB₂ powder obtained by milling with the 5 and 9 mm diameter balls for 50 h was approximately 370 nm.

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1. Introduction

Six types of binary niobium borides Nb₃B₂, NbB, Nb₅B₆, Nb₃B₄, NbB₂¹ and Nb₂B₃² have been reported. The diboride NbB₂ (AlB₂ type, Hexagonal) have high melting point, high hardness, high electric conductivity³ and superconductivity.⁴

NbB₂ has the potential for structural applications which require high temperature strength under severe conditions. In addition, it is reported that the NbB₂–CrB₂ composite has a high hardness and oxidation resistance.⁵

Many processes are available for the production of NbB₂ such as the solid-state reaction method,^{6,7} the thermal reduction of the oxide with boron,⁸ the arc melting method,⁹ the chemical vapor deposition method¹⁰ and the molten metallic solution method.¹¹ Mechanochemical approaches to prepare high melting point compounds such as MoB₂,¹² CrB₂,^{13,14} TiB₂,^{15–17} TiN¹⁷ and TiC¹⁷ were recently proposed which involves the ball-milling of an elemental powder mixture without external heat application. Morris and Morris¹⁴ reported the formation and amorphization of the

chromium borides and niobium borides by the ball milling of the elemental powder mixtures.

In this study, a powder mixture of Nb-B (1:2) was milled using different sizes milling balls in a planetary ball mill, and the effect of the ball size on the preparation of NbB₂ was examined.

2. Experimental

Metal niobium powder (99.9%, 45 μm) and amorphous boron powder (96.4%, 0.8 μm) were used as the starting material. A powder mixture of niobium and amorphous boron in 1:2 atomic ratio was milled using a planetary ball mill (Fritsch, Pulverisette 6) for 5–50 h at 600 rpm. For the milling, balls with diameters of 5, 9 or 16 mm were used and the effect of the ball size on the preparation of the NbB₂ was examined. We used a stainless steel vial and milling media. The balls to powder weight ratio was 20:1. The powder mixture and the balls were placed in a vial in a glovebox filled with argon gas. The as-milled powder was characterized by X-ray diffraction (Rigaku, rint 2500 V, 40 kV, 300 mA) with Cu Kα1 which was monochromatized by a fully automatic monochrometer.

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The obtained NbB_2 powder was characterized by a light-scattering instrument (Coulter, LS-230) for the average particle size analysis and the X-ray line broadening method was employed for the crystallite size measurement.

3. Results and discussion

3.1. Formation of NbB_2

The X-ray diffraction patterns of the product obtained by milling the powder mixture of Nb-B (1:2) using 5 mm diameter balls is shown in Fig. 1. Boron was not detected in the starting powder mixture. Only the X-ray diffraction peaks of niobium were observed in the milling for 5 h, but the peaks shifted to lower angles. The main peak of niobium (1 1 0) was separated into two parts, indicating a small diffraction peak on the lower angle side, and a similar separation was observed for the other peaks as well. It is postulated that this is due to boron dissolving in the niobium and the Nb-B solid solution was formed. After 5 h of milling, the lattice parameter of niobium was $a=0.3312$ nm. This value is approximately 0.2% greater than that of niobium.¹⁸ The increase in the lattice parameter indicates the diffusion of boron into the niobium. For the 10 h milling, the diffraction peaks of niobium became broad and the peaks shifted to a lower angle, but the formation of NbB_2 was not observed. By milling for 20 h, broad peaks of NbB_2 were observed, indicating that NbB_2 started to form, but niobium and boron remained. For the 50 h milling,

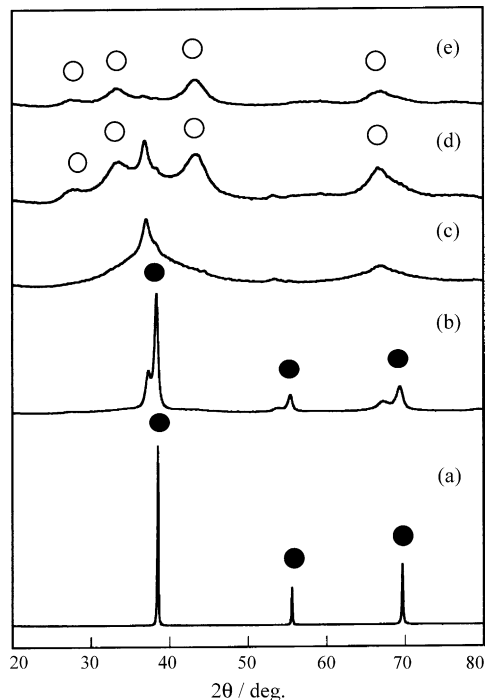


Fig. 1. X-ray diffraction patterns of Nb-B (1:2) mixture milled for (a) 0 h, (b) 5 h, (c) 10 h, (d) 20 h and (e) 50 h. Diameter of ball: 5 mm, (●) Nb and (○) NbB_2 .

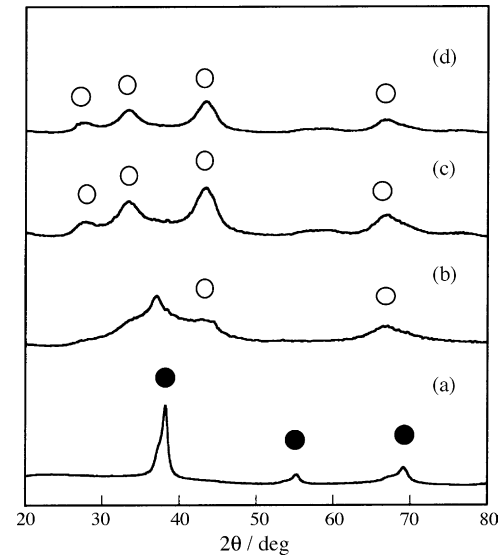


Fig. 2. X-ray diffraction patterns of Nb-B (1:2) mixture milled for (a) 5 h, (b) 10 h, (c) 30 h and (d) 40 h. Diameter of ball: 9 mm, (●) Nb and (○) NbB_2 .

the peaks of niobium disappeared and a single phase of NbB_2 was formed. The peaks of the formed NbB_2 were broad and the obtained NbB_2 powder can be estimated to have fine crystallites.

The X-ray diffraction patterns of the product obtained by milling the powder mixture of Nb-B (1:2) using 9 mm diameter balls are shown in Fig. 2. After the milling for 5 h, only the peaks of niobium were observed, which tended to be separated similar to the case of milling with 5 mm diameter balls. After the milling for 10 h, the intensity of niobium peaks decreased and very weak NbB_2 peaks were observed. After the milling for over 30 h, a single phase of NbB_2 was formed.

The X-ray diffraction patterns of the product obtained by milling the powder mixture of Nb-B (1:2) using 16 mm diameter balls is shown in Fig. 3. After the milling for 5 h, strong niobium and very weak NbB_2 peaks were observed, so it can be suggested that NbB_2 formation has begun. For the 10 h milling, the intensity of the peaks of niobium decreased and broad NbB_2 peaks were observed. After the milling for over 20 h, a single phase of NbB_2 was formed.

The relation between the ball size and the starting time of the NbB_2 formation is shown in Table 1. For the milling with the 5, 9 and 16 mm balls, the starting time of the NbB_2 formation was 20, 10 and 5 h, respectively. It can be seen that

Table 1
Relation between the time required for formation of the NbB_2 and the size of balls

Diameter of ball (mm)	NbB_2 formation (h)	Formation of single phase (h)
5	20	50
9	10	30
16	5	20

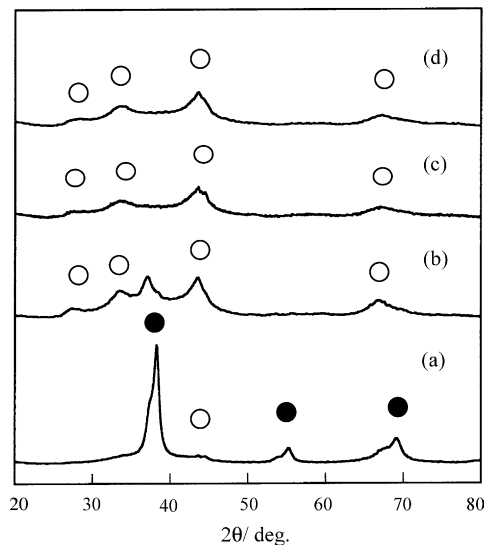


Fig. 3. X-ray diffraction patterns of Nb-B (1:2) mixture milled for (a) 5 h, (b) 10 h, (c) 20 h and (d) 40 h. Diameter of balls: 16 mm, (●) Nb and (○) NbB₂.

the larger the balls used, the earlier the starting time of the NbB₂ formation.

In addition, as the ball size increased, the time required for the formation of the single phase NbB₂ become shorter. In the mechanochemical process, the solid-state reaction is accelerated by applying a mechanical energy to the powder through milling of the powder mixture. The mechanical energy applied to the powder by the impact is greater as the ball size increase. The solid-state reaction is accelerated and the required formation time is supposed to be shortened.

3.2. Lattice parameter and particle size

The lattice parameter of NbB₂ obtained by milling the powder mixture of Nb-B (1:2) for 50 h with balls of 5, 9 and 16 mm diameter were $a=0.3103$ nm, $c=0.3286$ nm; $a=0.3095$ nm, $c=0.3279$ nm; $a=0.3114$ nm, $c=0.3250$ nm. The lattice parameters of NbB₂ after 50 h of milling, which was annealed at 1000 °C in an argon atmosphere for 1 h, was independent on the ball size, $a=0.3112$ nm, $c=0.3276$ nm. Brewer et al.⁶ reported the lattice parameters of $a=0.3110 \pm 0.0002$ nm, $c=0.3264 \pm 0.0002$ nm for NbB₂ prepared by the solid-state reaction. Okada et al.¹¹ reported the lattice parameters of NbB₂ single crystal prepared by the aluminum flux method; $a=0.3110 \pm 0.0001$ nm, $c=0.3284 \pm 0.0002$ nm and $a=0.3102 \pm 0.0001$ nm, $c=0.3321 \pm 0.0002$ nm for the chemical compositions of NbB_{1.90} and NbB_{1.96}, respectively. The lattice parameter of NbB₂ obtained in this study are in good agreement with those previously reported.

The average particle and the crystallite size of the NbB₂ powder obtained by milling the powder mixture of Nb-B (1:2) for 50 h are shown in Table 2. A very fine NbB₂ powder was obtained by milling with 5 and 9 mm diameter balls, which

Table 2

Average particle size and crystallite size of NbB₂ powder obtained by 50 h milling

Diameter of ball (mm)	Average particle size (nm)	Crystallite size (nm)
5	370	6.1
9	370	6.2
16	980	5.9

had the average particle size of approximately 370 nm, and a crystallite size of approximately 6.1–6.2 nm. On the other hand, the average particle size of the NbB₂ powder milled with the 16 mm diameter balls was approximately 980 nm. When a certain weight of balls are used, it is considered that the number of contact points between the balls and the powder may increase as the ball size decreases, so a finer powder could be obtained.

4. Summary

A powder mixture of Nb-B (1:2) was milled with balls of 5, 9 or 16 mm diameter, and the effect of the ball size on the preparation of NbB₂ was examined.

When milled with balls of 5, 9 and 16 mm diameters, the starting time of the NbB₂ formation was 20, 10 and 5 h, respectively, and the single phase of NbB₂ was obtained in 50, 30 and 20 h, respectively.

The lattice parameters of the obtained NbB₂ were $a=0.3112$ nm, $c=0.3276$ nm, which is in good agreement with that of previously reported. A very fine NbB₂ powder with the average particle size of approximately 370 nm and crystallite size of approximately 6.2 nm was obtained by milling with balls of 5 and 9 mm diameters for 50 h.

Although the time required for the formation of NbB₂ is longer as the ball size decreases, a finer NbB₂ powder is obtained.

References

- Massalski, T. B. ed., *Binary Alloy Phase Diagrams*, vol. 1. 2nd ed. ASM International, 1996, pp. 505–506.
- Okada, S., Hamano, K., Lundström, T. and Higashi, I., Crystal growth of the new compounds NbB, Nb₅B₆, Nb₃B₄, and NbB₂, using the copper-flux method. *AIP Conf. Proc.*, 1991, **23**, 456–459.
- Kieffer, L. and Benesovsky, F., *Hartstoffe*. Springer-Verlag, Wien, 1963, pp. 1–43.
- Klesnar, H., Aselage, T. L., Venturini, E. L., Emin, D., Newcomer, P. P. and Morosin, B., Superconductivity in niobium and molybdenum diborides. In *Proceedings of the 11th International Symposium on Boron, Borides and Related Compounds, Tsukuba 1993*, *Jpn. J. Appl. Phys. Series 10*, 1994, pp. 152–153.
- Talmy, I. G., Wuchina, E. J., Zaykoski, J. A. and Opeka, M. M., Properties of ceramics in the NbB₂–CrB₂ system. *Ceram. Eng. Sci. Proc.*, 1996, **3**, 128–135.
- Brewer, L., Sawyer, D. L., Templeton, D. H. and Dauben, C. H., A study of the refractory borides. *J. Am. Ceram. Soc.*, 1951, **34**, 173–179.

7. Matsudaira, T., Itoh, H. and Naka, S., Synthesis of niobium boride powder by solid state reaction between niobium and amorphous boron. *J. Less-Common Met.*, 1989, **155**, 207–214.
8. Peshev, P., Leyarovska, L. and Bliznakov, G., On the borothermic preparation of some vanadium, niobium and tantalum borides. *J. Less-Common Met.*, 1968, **15**, 259–267.
9. Lundström, T., Lönnberg, B. and Westman, I., A study of the microhardness in the homogeneity ranges of NbB₂ and TaB₂. *J. Less-Common Met.*, 1984, **96**, 229–235.
10. Armas, B., Combescure, C. and Trombe, F., Chemical vapor deposition of NbB₂ and TaB₂ through heating by concentration of solar radiation. *J. Electrochem. Soc. Solid-State Sci. Technol.*, 1979, 308–310.
11. Okada, S., Atoda, T. and Takahashi, Y., Preparation of NbB₂, TaB and TaB₂ single Crystals using molten aluminum flux. *J. Chem. Soc. Jpn.*, 1985, **1985**, 1535–1543.
12. Kudaka, K., Iizumi, K., Sasaki, T. and Okada, S., Mechanochemical synthesis of MoB₂ and Mo₂B₅. *J. Alloys Compd.*, 2001, **315**, 104–107.
13. Iizumi, K., Kudaka, K., Maezawa, D. and Sasaki, T., Mechanochemical synthesis of chromium borides. *J. Ceram. Soc. Jpn.*, 1999, **107**, 491–493.
14. Morris, M. A. and Morris, D. G., Ball-milling of elemental powders—compound formation and/or amorphization. *J. Mater. Sci.*, 1991, **26**, 4687–4696.
15. Calka, A. and Radlinski, A. P., Formation of TiB₂ by mechanical alloying. *J. Less-Common Met.*, 1990, **161**, 23–26.
16. Yong Ho, P., Hashimoto, H., Nakamura, M., Abe, T. and Watanabe, R., Phase evolution and forming process of compound during ball milling of a mixture of Ti and B powder. *Nippon Kinzoku Gakkai*, 1993, **57**, 952–956.
17. Kudaka, K., Iizumi, K. and Sasaki, T., Mechanochemical syntheses of titanium carbide, diboride and nitride. *J. Ceram. Soc. Jpn.*, 1999, **107**, 1019–1024.
18. International Center for Diffraction Data 35-0789.