SYNTHESIS OF NIOBIUM BORIDE POWDER BY SOLID STATE REACTION BETWEEN NIOBIUM AND AMORPHOUS BORON*

TSUNEAKI MATSUDAIRA, HIDEAKI ITOH and SHIGEHARU NAKA

Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 (Japan)

HIROSHI HAMAMOTO

Toyota Central Research and Development Laboratories, Inc. Nagakute-cho, Aichi Pref. 480-11 (Japan)

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Summary

Niobium boride powders were synthesized by solid state reaction between niobium metal powder and amorphous boron powder. The formation of niobium borides was found to be dependent on temperature. Single phases of the stable borides, NbB and NbB₂, were formed by heating mixed powders corresponding to the stoichiometric compositions at 1000 °C for 60 min. A single phase of Nb₃B₄ was obtained at a higher temperature of 1800 °C as a result of the promoted diffusion of boron atoms in niobium metal. All synthesized powders were well dispersed and had particle sizes of 5 - 10 μ m. The sinterability of the synthesized NbB₂ powder was evaluated at high pressure (4 GPa) and temperature (1600 °C) for 15 min; a singlephase sintered compact of NbB₂ was formed with a relative density of 98% and a Vickers microhardness of 2600 kg mm⁻².

1. Introduction

Five niobium boride compounds $(Nb_2B, Nb_3B_2, NbB, Nb_3B_4$ and $NbB_2)$ are present in the Nb-B system [1 - 3]. They have high melting points and microhardness and good electrical and thermal conductivities. There are relatively few studies available on the synthesis of niobium boride powders compared with investigations of other transition metal borides. The main methods of preparation of niobium boride are the solid state reaction between niobium and boron and molten salt electrolysis [4 - 9]. However, investigations of the solid state reaction have been confined to temperatures

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above 1500 $^{\circ}$ C. The preparation conditions and formation behaviour of niobium boride powder have not been reported for the lower temperature range.

The heat of formation of niobium boride lies between those of the IVa transition metal borides and VIa transition metal borides [10]. For the solid state reaction between titanium metal and amorphous boron, rapid formation of titanium boride occurs and the reaction must be controlled [11 - 13]. By contrast, activation pretreatment in hydrogen is required to enhance the formation of tungsten boride [14, 15]. The rate of formation of niobium boride can be estimated by reference to the investigations mentioned above.

In this work, the preparation conditions of various niobium boride powders were studied. Mixtures of niobium powder and amorphous boron powder were heated in the temperature range 600 - 1800 °C. The synthesized niobium boride powders were characterized. The synthesized NbB₂ powder was sintered at high pressure and temperature and the results are reported in this paper.

2. Experimental details

2.1. Synthesis of niobium boride powder

The starting materials used for the preparation of niobium boride powders were niobium metal powder (High Purity Chemicals Co.; average particle size, 8 μ m; purity, better than 99 wt.%) and amorphous boron powder (Rare Metallic Co.; average particle size, 0.9 μ m; purity, 96.6 wt.%). As-received amorphous boron powder contained volatile impurities (H₂O, oxygen, etc. (2.4 wt.%)) and metal impurities (magnesium, aluminium, iron, silicon, etc. (1.0 wt.%)). The net boron content (96.6 wt.%) in the asreceived amorphous boron powder was used for the calculation of the atomic ratio B:Nb.

As-received niobium and amorphous boron powders were degassed separately at 600 °C for 60 min in vacuum (5×10^{-5} Torr) to eliminate the adsorbed gaseous species. The powder, which was mixed in an agate mortar in the atomic ratios B:Nb = 0.25 - 2.0, was treated at 600 - 1800 °C for 60 min in a stream of argon (flow rate, 50 ml min⁻¹). The effect of pretreatment at 600 °C for 60 min in an H₂-Ar stream was examined.

2.2. Analysis of the treated powder

The treated specimen was identified by X-ray diffraction. The relative amounts and crystallinity of the crystalline phases in the specimen were evaluated using the normalized intensities of the selected diffraction lines. The lines for evaluation were 110 for niobium, 211 for Nb₂B, 201 for Nb₃B₂, 021 for NbB, 110 for Nb₃B₄, 101 for NbB₂ and 111 for NbH. Normalized relative intensities were determined using the peak height ratio $I:I_{\rm Si}$, where $I_{\rm Si}$ shows the intensity of the 200 line of a given amount of silicon (purity, 99.99 wt.%) which was added to the specimen. The grain shape and grain size of the synthesized powder were examined by scanning electron microscopy (SEM). The oxygen content in the specimen was measured using electron probe microanalysis (EPMA).

2.3. Sintering of the synthesized powder

Two types of powder were synthesized for the evaluation of sinterability: one had the stoichiometric composition NbB₂ and the other contained 20 at.% of amorphous boron in excess of the stoichiometric composition. The latter is formulated as NbB₂ + 0.2B. The stoichiometric NbB₂ powder and the NbB₂ + 0.2B powder mixed with 10 at.% niobium metal powder ((NbB₂ + 0.2B) + 0.1Nb) were moulded at 20 MPa at room temperature. The green compacts were subsequently sintered at 4 GPa and 1600 °C for 15 min using a girdle-type high pressure apparatus.

The sintered density was measured using Archimedes' method. The Vickers microhardness of the sintered compact was measured under a load of 200 gf. The fractured surface of the specimen was observed using SEM.

3. Results and discussion

3.1. Formation behaviour of niobium borides at various starting compositions

Figures 1 and 2 show the dependence of the relative X-ray intensities of the species formed on the atomic ratios B:Nb of the starting mixed powders when the specimens are treated for 60 min in an argon stream at 1000 °C and 1800 °C respectively. The B:Nb values of the specimens range between 0.25 and 2.0. NbB, Nb₃B₄ and NbB₂ are formed by the heat treatment at 1000 °C (see Fig. 1). Single phases of the stable borides NbB and NbB₂ are



Fig. 1. Relationship between the relative intensities of the niobium boride phases and the atomic ratio B:Nb of the starting powder (treatment conditions: 1000 °C, 60 min): \circ , Nb; \Box , NbB; \diamond , Nb₃B₄; \diamond , NbB₂.

Fig. 2. Relationship between the relative intensities of the niobium boride phases and the atomic ratio B:Nb of the starting powder (treatment conditions: 1800 °C, 60 min): \triangle , Nb₂B; \bigtriangledown , Nb₃B₂; \Box , NbB; \diamondsuit , Nb₃B₄; \diamondsuit , NbB₂.

formed by the heat treatment of specimens with the exact stoichiometric compositions (B:Nb = 1.0 and B:Nb = 2.0 respectively). The intensity of Nb₃B₄ is smaller than that of NbB even at the stoichiometric composition of Nb₃B₄ (B:Nb = 1.3), where a large amount of NbB coexists with Nb₃B₄. At the higher reaction temperature (1800 °C) (see Fig. 2), the formation behaviour of NbB and NbB₂ resembles that of the reaction at 1000 °C. For the compositions B:Nb < 1.0, however, the lower borides Nb₂B and Nb₃B₂ are observed instead of the coexistence of unreacted niobium metal. Boron diffusion into niobium metal is enhanced at the elevated reaction temperature of 1800 °C. A single phase of Nb₃B₄ is obtained by treatment of the stoichiometric composition B:Nb = 1.3. These results suggest that the formation behaviour of niobium boride is very dependent on the reaction temperature as well as on the composition of the specimen.

3.2. Effect of reaction temperature

Figure 3 shows the dependence of the relative intensities of the species formed on the reaction temperature when the mixed powder with the atomic ratio B:Nb = 1.0 is treated in the temperature range 600 - 1800 °C for 60 min in an argon stream. At the reaction temperature of 600 °C, niobium remains unreacted, with no formation of niobium boride. Amorphous boron is not detected by X-ray diffraction. NbB₂ and NbB are formed at 700 °C and 900 °C respectively. The intensity of NbB₂ has a maximum value at 800 °C. The intensity of niobium decreases, whereas that of NbB increases, with increasing reaction temperature in the range 800 - 1000 °C. A single phase of NbB is obtained at 1000 °C. The intensity of NbB is fairly constant at temperatures above 1000 °C.

Figure 4 shows the dependence of the relative intensities of the species formed on the reaction temperature for the specimen with the atomic ratio



Fig. 3. Variation in the relative intensities of the species formed as a function of the reaction temperature (atomic ratio of the mixed powder, B:Nb = 1.0; holding time, 60 min): \bigcirc , Nb; \square , NbB; \bigcirc , NbB₂.

Fig. 4. Variation in the relative intensities of the species formed as a function of the reaction temperature (atomic ratio of the mixed powder, B:Nb = 1.3; holding time, 60 min): \circ , Nb; \Box , NbB; \diamond , Nb₃B₄; \diamond , NbB₂.

B:Nb = 1.3. NbB₂ and NbB are formed at 700 °C and 900 °C respectively in a similar manner as shown in Fig. 3. The formation of Nb₃B₄ is initiated at 1000 °C with a simultaneous disappearance of niobium metal. The intensity of Nb₃B₄ increases above 1000 °C and that of NbB decreases gradually. Treatment at 1800 °C is required for the formation of a single phase of Nb₃B₄.

Figure 5 shows an analogous diagram of the relative intensity vs. reaction temperature for the atomic ratio B:Nb = 2.0. The formation of NbB₂ is initiated at 700 °C. The intensity of NbB₂ increases and that of niobium decreases with increasing reaction temperature without formation of any other niobium boride. A single phase of NbB₂ is formed at 1000 °C. The intensity of NbB₂ increases slightly from 1000 °C to 1400 °C and remains constant above 1400 °C.

This dependence of boride formation on temperature in the Nb-B system may be due to the fact that the crystal structures of NbB and NbB₂ are very simple and stable [1] and these compounds are easily formed at relatively low temperatures. A single phase of Nb₃B₄ is formed at 1800 °C due to the promoted diffusion of boron in niobium metal.

3.3. Effect of pretreatment

Figure 6 shows the dependence of the relative intensities of the species formed on the reaction temperature, when the mixed powder with the atomic ratio B:Nb = 2.0 is pretreated at 600 °C for 60 min in an H₂-Ar stream (niobium hydride (NbH) is formed and no niobium metal remains). The pretreated powder is subsequently heat treated in the temperature range 600 - 1800 °C for 60 min in an argon stream. At the reaction temperature of 600 °C in argon, a large amount of NbH decomposes and niobium metal is obtained. The intensities of reformed niobium and NbH decrease and that of



Fig. 5. Variation in the relative intensities of the species formed as a function of the reaction temperature (atomic ratio of the mixed powder, B:Nb = 2.0; holding time, 60 min): \circ , Nb; \diamond , NbB₂.

Fig. 6. Variation in the relative intensities of the species formed as a function of the reaction temperature (atomic ratio of the mixed powder, B:Nb = 2.0; holding time, 60 min; pretreatment conditions, 600 °C for 60 min in H_2 -Ar): \circ , Nb; \diamond , NbB₂; \diamond , NbH.

NbB₂ increases with increasing temperature up to 1000 °C. The temperature of formation of NbB₂ after pretreatment is the same as that of NbB₂ without pretreatment (*cf.* Figs. 5 and 6). However, EPMA of the synthesized powders reveals a difference in the oxygen content of the powders with and without pretreatment. The oxygen contents in the synthesized powders with and without pretreatment are 0.4 wt.% and 1.0 wt.% respectively. Therefore pretreatment in H₂-Ar reduces the oxygen content of the synthesized powders.





Fig. 7. Scanning electron micrographs of NbB₂ powder: (a) pretreated at 600 °C for 60 min in H₂-Ar, followed by treatment at 1000 °C for 60 min in argon; (b) treated at 1000 °C for 60 min in argon.

Figures 7(a) and 7(b) show scanning electron micrographs of NbB₂ powders with and without pretreatment respectively. Both powders were synthesized at 1000 °C for 60 min. The particle size of the powders is 5 - 10 μ m, which is almost the same as that of the initial niobium metal powder. When reformed niobium metal is pulverized and used as the starting niobium powder no effect is observed.

3.4. Sinterability of the synthesized powders

Two types of powder were sintered: NbB₂ powder and (NbB₂ + 0.2B) + 0.1Nb. Both specimens have the stoichiometric composition NbB₂. Figure 8 shows scanning electron micrographs of the fractured surfaces of the compacts sintered at high pressure (4 GPa) and temperature (1600 °C) for 15 min. The sintered compact without addition of niobium (see Fig. 8(a)) contains many micropores. The sintered density is 6.30 g cm⁻³ (90%)





Fig. 8. Scanning electron micrographs of the fractured surfaces of the compacts sintered at 4 GPa and 1600 °C for 15 min. Starting powder: (a) NbB₂; (b) (NbB₂ + 0.2B) + 0.1Nb.

of the theoretical value). The effect of niobium addition on the microstructure of the sintered compact is quite significant as shown in Fig. 8(b). The number of micropores decreases and the sintered density increases up to 6.85 g cm^{-3} (98% of the theoretical value). A high value of microhardness (2600 kg mm⁻²) is obtained.

It is confirmed that the sinterability is increased by the addition of 10 at.% niobium metal powder to $(NbB_2 + 0.2B)$. No niobium metal phase is identified by X-ray diffraction even in the specimen with added niobium. The densification of the compact is promoted by reaction sintering, which is accompanied by the formation of NbB₂ from amorphous boron and added niobium.

4. Conclusions

Various niobium boride powders were synthesized by solid state reaction between niobium and amorphous boron powders. The preparation conditions and powder sinterability of niobium boride were investigated.

(i) The formation of niobium borides was found to be dependent on temperature. Single phases of NbB and NbB₂ were formed using powders of the correct stoichiometric compositions by heating at 1000 °C for 60 min. A single phase of Nb₃B₄ was obtained at 1800 °C as a result of the promoted diffusion of boron in niobium metal.

(ii) The oxygen content of the synthesized powder was decreased by pretreatment at 600 °C for 60 min in an H_2 -Ar stream.

(iii) The synthesized powder was well dispersed and had a particle size of 5-10 μ m. A single-phase sintered compact of NbB₂ with a relative density of 98% and a microhardness of 2600 kg mm⁻² was prepared by sintering the specimen (NbB₂ + 0.2B) + 0.1Nb at 4 GPa and 1600 °C for 15 min.

References

- 1 H. Nowotny, F. Benesovsky and R. Kieffer, Z. Metallkd., 50 (1959) 417.
- 2 G. V. Samsonov and I. M. Vinitskii, Handbook of Compounds, IFI/Plenum, New York, 1980, pp. 40, 143, 184.
- 3 T. Lundstrum, Boron and Refractory Borides, Springer, Berlin, 1977, p. 351.
- 4 L. Andrieux, C. R. Acad. Sci., 189 (1929) 1279.
- 5 J. T. Norton, H. Blumenthal and J. Sindeband, Trans. AIME, 185 (1959) 749.
- 6 L. Brewer, D. L. Sawyer, D. H. Templeton and C. H. Dauben, J. Am. Ceram. Soc., 34 (1951) 173.
- 7 F. W. Gleser, J. Met., 4 (1952) 391.
- 8 L. H. Anderson and R. Kiessling, Acta Chem. Scand., 4 (1950) 160.
- 9 L. H. Anderson and R. Kiessling, Acta Chem. Scand., 4 (1950) 209.
- 10 JANAF Thermochemical Tables, National Bureau of Standards, Washington DC, 2nd edn., June 1971, pp. 191, 193.
- 11 T. Matsudaira, H. Itoh, S. Naka and H. Hamamoto, Funtai Oyobi Funmatsuyakin, 35 (1988) 229.
- 12 H. Itoh, T. Matsudaira, S. Naka and H. Hamamoto, J. Mater. Sci., 24 (1989) 420.
- 13 T. Matsudaira, H. Itoh, S. Naka, H. Hamamoto and M. Obayashi, J. Mater. Sci., 23 (1988) 288.
- 14 T. Matsudaira, H. Itoh, S. Naka, H. Hamamoto and M. Obayashi, Zairyo, 36 (1987) 1167.
- 15 H. Itoh, T. Matsudaira, S. Naka, H. Hamamoto and M. Obayashi, J. Mater. Sci., 22 (1987) 2811.