JOURNAL OF MATERIALS SCIENCE 22 (1987) 2811–2815

Formation process of tungsten borides by solid state reaction between tungsten and amorphous boron

H. ITOH, T. MATSUDAIRA, S. NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

H. HAMAMOTO, M. OBAYASHI
Toyota Central Research and Development Laboratories, Inc., Nagakute-cho, Aichi Pref. 480-11, Japan

Various kinds of tungsten borides were synthesized by solid state reaction between tungsten and amorphous boron powders. The mixed powders with various compositions (B/W = 0.4 to 13.0) were treated at 800 to 1550° C for 0 to 120 min in a stream of argon. Four kinds of boride phases such as W_2B, WB, W_2B_5 and WB_4 were formed, although the boride phase having the composition of the highest boride, WB_{12}, did not appear. The formation of W_2B was initiated approximately at 1000° C in excess of tungsten content. On the other hand, in the excess boron content, the formation of WB, W_2B_5 and WB_4 was initiated approximately at 800, 950 and 1200° C, respectively. The maximum formation amount and crystallinity of WB and W_2B_5 was found in nearly 10 at% excess boron content in their own stoichiometric compositions. The only crystalline phase of WB_4 was prepared with a large excess boron content. However, the formation behaviour of WB_4 showed that WB_4 is metastable above 1400° C. The stability of WB_4 phase could be increased by the presence of excess boron.

1. Introduction

Tungsten borides are known to have high values of hardness, chemical inertness and electronic conductivity [1]. They have possible industrial applications to abrasive, corrosion-resistant and electrode materials which are exposed to particular environments. Various kinds of borides such as W_2B, WB, WB_2, W_2B_5, WB_4 and WB_{12} were known to exist in the W–B system [1, 2]. These borides have been synthesized by solid state reaction [2, 3], reduction of oxides by carbon [4], molten salt electrolysis [5] and chemical vapour deposition [6–8]. Synthesis by solid state reaction between tungsten and boron powders is an appropriate method to control the well-defined stoichiometries of the synthesized borides. The synthesis of borides by the direct combination of elements was reported by Portnoy *et al.* [2] and Bodrova *et al.* [3]. These borides were prepared at high temperatures, above 1700° C, in vacuum or in argon atmosphere. However, their formation processes were not described.

In the present work, various kinds of borides in the W–B system were synthesized by the solid state reaction between tungsten and amorphous boron. The formation process and phase stability of each boride were examined as a function of the treatment temperature and time, and atomic ratio of boron to tungsten.

2. Experimental procedure

2.1. Preparation of tungsten borides

The starting materials for the preparation of tungsten borides were as follows: tungsten powder (Nihon Sinkinzoku Co., average particle size 0.5 μm, purity > 99.9%) and amorphous boron powder (Rare Metallic Co., average particle size 0.9 μm, purity 96.6%).

In order to eliminate the contaminations or adsorbed gaseous species, tungsten and amorphous boron powders in alumina boats were pretreated separately at 600° C for 60 min in vacuum (5×10^{-5} torr) and subsequently at 600° C for 60 min in a stream of hydrogen (flow rate 50 ml min^{-1}). The powder which was mixed in an agate mortar at various atomic ratios of B/W, was further pretreated at 500° C for 60 min in a stream of hydrogen. The mixed pretreated powder was finally treated at 800 to 1550° C for 0 to 120 min in a stream of argon (flow rate 50 ml min^{-1}).

2.2. Analysis of treated specimens

The treated specimens were identified by X-ray diffraction. The relative amount and crystallinity of the crystalline phase in the specimens were evaluated by the normalized intensities of selected diffraction lines. The lines for evaluation were 1 1 0, 2 1 1, 0 2 1, 0 0 4 and 1 0 1, respectively, for W, W_2B, WB, W_2B_5 and WB_4. Normalized relative intensity was determined by the peak height ratio (I/I_{NaCl}), where I_{NaCl} is the intensity of the 2 0 0 line of sodium chloride.

Lattice parameters of boride compounds were measured using silicon (purity 99.99%) as an internal standard. Lattice spacings, measured from the 2 1 5

0022–2461/87 $03.00 + .12

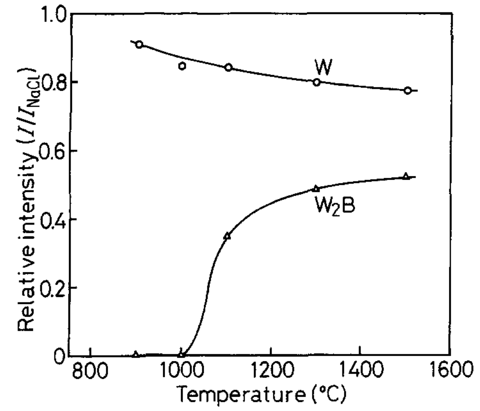

Figure 1 Relationship between the relative intensity of reaction species and treatment temperature with the holding time of 15 min. Atomic ratio of the mixed powder: B/W = 0.4

and 2 0 8 lines of WB, were corrected by that from the 3 3 1 line of silicon. Lattice spacings from the 1 1 4 and 1 0 9 lines of W_2B_5 were corrected by that from the 4 0 0 line of silicon. All the lattice spacings of WB_4 were corrected by those from the 1 1 1, 3 1 1 and 3 3 1 lines of silicon, from which the lattice parameters of WB_4 were calculated using Cohen's method [9].

The average grain size of the treated specimen powder was examined by scanning electron microscopy (SEM).

The atomic ratio of B/W was measured by inductively coupled plasma (ICP) emission analysis. An appreciable difference in composition could not be found before and after the final treatment of every specimen.

3. Results and discussion

3.1. Effect of treatment temperature on boride formation

Two kinds of pretreated mixed powders with different atomic ratios (B/W = 0.4 and 7.0) were heated at 800 to 1550° C for 15 min. Figs 1 and 2 show the relationships between the relative diffraction intensities of the reaction species and the treatment temperature at the atomic ratios of B/W = 0.4 and 7.0, respectively.

Fig. 1 shows the results at the atomic ratio of B/W = 0.4, which contains tungsten in excess of the tungsten content in the lowest boride W_2B. No boride formation was observed at temperatures below 1000° C; only tungsten was detected. Amorphous boron could not be detected by X-ray diffraction. The formation of W_2B is initiated approximately at 1000° C. The relative intensity of W_2B increases up to 1500° C with a gradual decrease in the intensity of tungsten. Other higher borides could not be formed even at 1500° C.

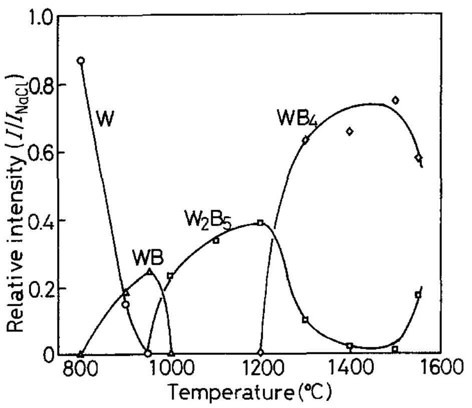

Figure 2 Relationship between the relative intensity of reactive species and treatment temperature with the holding time of 15 min. Atomic ratio of the mixed powder: B/W = 7.0.

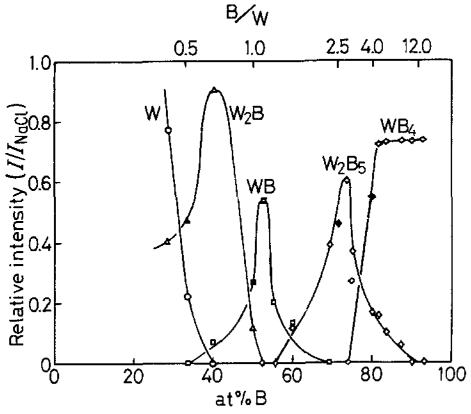

Figure 3 Relationship between the relative intensity of W–B compounds and boron content (at % B) or the atomic ratio of B/W at 1400° C for 60 min: (○) W, (△) W_2B, (□) WB, (◇) W_2B_5, (◇) WB_4. Solid symbols show the relative intensity at stoichiometric composition of each W–B compound.

Higher borides such as WB, W_2B_5 and WB_4 were formed, as shown in Fig. 2, at the atomic ratio of B/W = 7.0, which contains boron in excess of the boron content in stoichiometric WB_4. The formation of WB was initiated at almost 800° C, with a decreasing intensity of tungsten. The only crystalline phase of WB was found at 950° C, above which W_2B_5 formed. At a higher temperature of 1000° C, an appreciable amount of W_2B_5 formed, and WB disappeared. The relative intensity of W_2B_5 passed through a maximum at 1200° C. WB_4 was formed at elevated temperatures above 1200° C with a decrease in the intensity of W_2B_5. The amount of formation and crystallinity of WB_4 had a maximum at 1400 to 1500° C, when a small amount of W_2B_5 coexisted with WB_4. In contrast, the amount of WB_4 decreased above 1550° C, with an increase in W_2B_5 formation instead. The formation behaviour of WB_4 will be described in Section 3.4.

W_2B appeared as the only boride phase in the heating process of the specimen with B/W = 0.4. Other higher borides (WB, W_2B_5 and WB_4) were formed at B/W = 7.0. This behaviour suggests that boride formation occurs by the diffusion of boron in tungsten. However, no detection of W_2B at the composition of B/W = 7.0 in Fig. 2, would be because the formation of higher borides, WB or W_2B_5 was favoured at temperatures below 1000° C. The boride formation was found, therefore, to be affected not only by the composition of the starting mixed powder, but also by the treatment temperature.

3.2. Effect of mixing atomic ratio on boride formation

Fig. 3 shows the dependence of the relative intensity of the reaction species on boron content (at % B), where various kinds of pretreated mixed powders were treated at 1400° C for 60 min. This treatment tem-

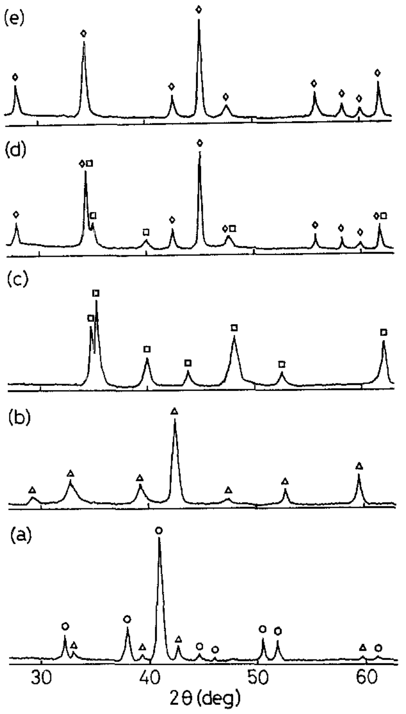

Figure 4 X-ray diffraction patterns of the specimens treated at 1400° C for 60 min: (○) W_2B, (△) WB, (□) W_2B_5, (◇) WB_4. (a) B/W = 0.67, (b) B/W = 1.1, (c) B/W = 2.75, (d) B/W = 4.5, (e) B/W = 9.0.

perature (1400° C) was chosen by reference to results in previous section. The composition of the specimens ranged from B/W = 0.4 (25 at % B) to B/W = 13.0 (92 at % B). Fig. 4 shows the X-ray diffraction patterns of the treated specimens having compositions of the atomic ratios B/W = 0.67, 1.1, 2.75, 4.5, 9.0.

In Fig. 3, the treated specimen at B/W = 0.4 (25 at % B) contained W_2B and unreacted tungsten as a crystalline phase. A maximum intensity of W_2B was found at B/W = 0.67 (40 at % B) accompanied by the disappearance of tungsten and the appearance of WB, as shown in Fig. 4a. W_2B always coexisted with tungsten or WB. The only crystalline phase of WB or W_2B_5 was formed at B/W = 1.1 to 1.2 (53 to 55 at % B) or B/W = 2.25 to 3.0 (69 to 75 at % B), respectively. The maximum intensity of WB or W_2B_5 was obtained at 10 at % boron in excess of the boron content in WB or W_2B_5. The corresponding X-ray diffraction patterns are shown in Figs 4b and c, respectively. WB_4 formed at B/W $\geqslant$ 3.0 (75 at % B), increasing the intensity to B/W = 4.5 (82 at % B). At higher atomic ratios, the intensity of WB_4 was kept nearly constant with that of W_2B_5 decreasing to zero at B/W = 9.0 (90 at % B). The X-ray diffraction patterns of B/W = 4.5 and 9.0 are shown in Figs 4d and e, respectively. The only crystalline WB_4 was prepared at higher boron contents B/W = 9.0 to 13.0 (90 to 93 at % B) when WB_{12} could not be detected. All the borides were found to form appropriately in excess of the boron content in their own stoichiometric compositions. These results verify that boride formation would be promoted by the presence of excess amounts of boron around the tungsten grains.

The existence of boride compounds, W_2B, WB, W_2B_5 and WB_{12} is shown in the phase diagram [2]. In the present work, three kinds of borides (W_2B, WB and W_2B_5) were confirmed. However, WB_4 was formed instead of WB_{12}. The formation of W_2B, WB and W_2B_5 was reported on diffusion coating of boron into tungsten metal in the temperature range 1100 to 1500° C using BCl_3 as the boron source [7, 8].

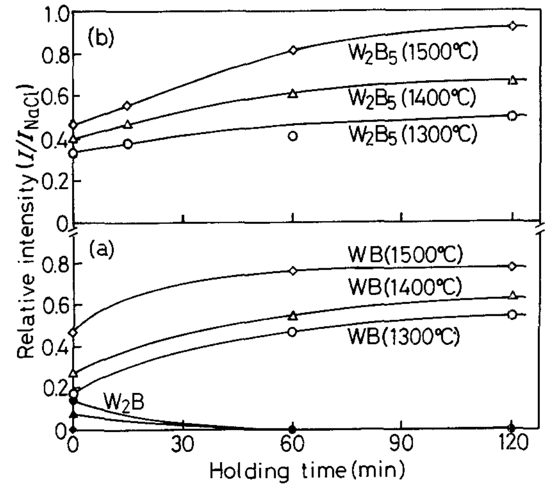

Figure 5 Variation of relative intensities of WB and W_2B_5 with holding time at various temperatures. Atomic ratio of the mixed powder: (a) B/W = 1.1, (b) B/W = 2.75.

3.3. Effect of holding time on the formation of WB and W_2B_5

Figs 5a and b show plots of the relative intensities of WB and W_2B_5 as a function of holding time (0 to 120 min) at temperatures in the range 1300 to 1500° C. The mixed powders of B/W = 1.1 and 2.75 were treated for the formation of WB and W_2B_5, respectively. In Fig. 5a, W_2B coexisted with WB even at a holding time of zero below 1400° C. WB, as the only crystalline phase, was obtained after a treatment time of over 60 min. On the other hand, the only crystalline phase of W_2B_5 was formed at the beginning of soaking at 1300° C with no detection of other boride phases, as shown in Fig. 5b. The relative intensities of both WB and W_2B_5 increased with holding time and temperature.

The lattice parameters of WB in the specimen treated at 1400° C for 60 min, were $a = 0.3126 \pm 0.0002$ nm and $c = 1.6901 \pm 0.0004$ nm, which agreed with the reported values ($a = 0.3128$ nm and $c = 1.6897$ nm) [11] in the tetragonal system. The lattice parameters of W_2B_5 in the specimen treated under the same conditions were $a = 0.2982 \pm 0.0002$ nm and $c = 1.3886 \pm 0.0004$ nm in agreement with the reported values ($a = 0.2984$ nm and $c = 1.3882$ nm) [12] in the hexagonal system.

The average grain sizes of the prepared powders of both WB and W_2B_5 were 0.5 to 1.0 μm. There was little difference in grain size between the prepared powders treated under above conditions.

3.4. Formation behaviour and phase stability of WB_4

Fig. 6 shows the dependence of the relative intensities of WB_4 and W_2B_5 on the holding time (0 to 120 min) at B/W = 4.5 for temperatures of 1300 to 1500° C. At the treatment temperature of 1300° C, the relative intensity of WB_4 increased gradually with holding time, accompanied by a slight decrease in that of

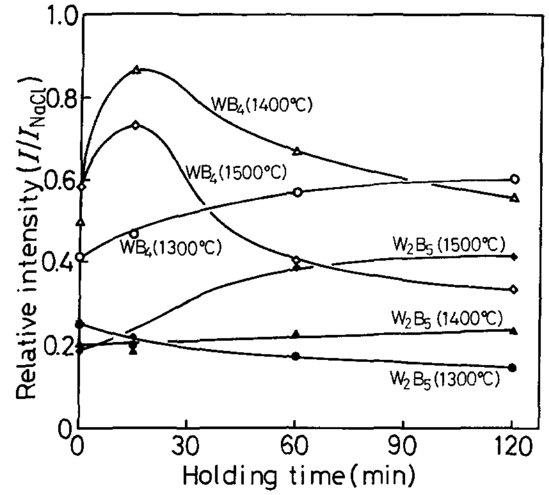

Figure 6 Variation of relative intensity of WB_4 and W_2B_5 with holding time at various temperatures. Atomic ratio of the mixed powder: B/W = 4.5.

W_2B_5. The lattice parameters of WB_4, which were formed at 1300° C for 120 min, were $a = 0.5199 \pm 0.0002$ nm and $c = 0.6336 \pm 0.0002$ nm in the hexagonal system. They agreed with the reported values [3].

In the case of treatments at 1400° C, a rapid increase in the amount of WB_4 formed was observed up to 15 min. The formation of WB_4 by boron diffusion into the core of the tungsten particle would prevail in the initial stage of treatment because of the high concentration gradient. Then, the relative intensity of WB_4 decreased after 15 min with holding time. At the elevated temperature of 1500° C, the amount of WB_4 decreased further, while the coexisting amount of W_2B_5 increased with holding time.

As shown in Fig. 3, the only crystalline phase of WB_4 was prepared in the mixed powder composition with a large excess (90 at %) of boron content for the atomic ratio B/W = 4.0. Therefore, the formation behaviour and phase stability of WB_4 were examined at the atomic ratio B/W = 7.0. Fig. 7 shows analogous plots of the relative intensities at the composition of B/W = 7.0. The amount of the coexisting phase W_2B_5 formed is depressed remarkably at 1300° C because of the presence of excess boron. Compared with the amount of WB_4 formed at 1400° C in Fig. 6, the stabilization behaviour of WB_4 in the presence of excess boron can be confirmed. At the elevated temperature of 1500° C, this stabilization behaviour could not be observed, but the amount of WB_4 formed was considerably decreased, similar to that in Fig. 6. This phenomenon of coexisting species such as WB_4 and W_2B_5 shows that WB_4 is a metastable phase above 1400° C. Consequently, the following relationship of coexisting phases would be valid:

$$2WB_4(s) \rightleftharpoons W_2B_5(s) + 3B(s).$$

The stability of the WB_4 phase must be increased in the presence of excess boron according to the law of mass action.

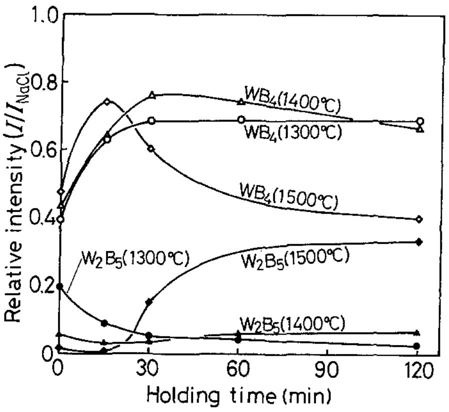

Figure 7 Variation of relative intensity of WB_4 and W_2B_5 with holding time at various temperatures. Atomic ratio of the mixed powder: B/W = 7.0.

4. Conclusion

Various boride compounds in the W–B system were synthesized by solid state reaction between tungsten and amorphous boron powders. The mixed powders with various compositions (B/W = 0.4 to 13.0) were pretreated at 500° C for 60 min in a stream of hydrogen and subsequently treated at 800 to 1500° C for 0 to 120 min in a stream of argon.

1. W_2B, WB, W_2B_5 and WB_4 were formed by varying the mixing ratio of B/W at 1400° C for 60 min. The highest boride phase, WB_{12}, did not appear.

2. The formation of W_2B was initiated at approximately 1000° C at the atomic ratio of B/W = 0.4, which contains tungsten in excess of the tungsten content in the lowest boride, W_2B. On the other hand, at the atomic ratio of B/W = 7.0, which contains excess boron of the boron content in WB_4, the formation of WB, W_2B_5 and WB_4 was initiated at 800, 950 and 1200° C, respectively.

3. The maximum formation amount and crystallinity of WB and W_2B_5 were found in nearly 10 at % excess of the boron content in their own stoichiometric compositions. The formation amounts of the only crystalline phase of WB or W_2B_5, were increased with the length of holding time and temperature.

4. The only crystalline phase of WB_4 was prepared at the composition of mixed powders in a large excess (B/W = 9.0) of boron content. However, WB_4 phase was found to show a metastable behaviour above 1400° C and to be stabilized in the presence of excess boron.

References

1. G. V. SAMSONOV and I. M. VINITSKII, "Handbook of Compounds" (IFI/Plenum, New York, 1980) pp. 40, 143 and 184.
2. K. I. PORTNOY, V. M. ROMASHOV and Y. V. LEVINSKY, *Porosh. Met.* (1967) 75.
3. L. G. BODROVA, M. S. KOVAL'CHENKO and T. I. SEREBRYAKOVA, *ibid.* (1974) 1.
4. L. LEYAROVSKA and E. LEYAROVSKI, *J. Less-Common Metals* **67** (1979) 249.
5. G. WEISS, *Ann. Chim.* **1** (1949) 318.
6. I. E. CAMPBELL, C. P. POWELL, D. H. NOWICKI and D. W. GONSER, *J. Electrochem. Soc.* **96** (1949) 318.
7. M. GEBHARDT, "Crystal Growth: An Introduction" (North-Holland, Amsterdam, 1973) p. 127.

8. G. V. SAMSONOV and A. P. EPIK, "Coating of High-Temperature Materials", Part 1 (Plenum, New York, 1966) p. 22.
9. B. D. CULLITY, "Elements of X-ray Diffraction" (Addison-Wesley, Reading, Massachusetts, 1956) p. 338.
10. T. MATSUDAIRA, H. ITOH, S. NAKA, H. HAMAMOTO and M. OBAYASHI, *Yogyo-Kyokai-Shi* **95** (1987) 248.
11. S. OKADA, M. SATOH and T. AGATA, *Nippon Kagaku Kaishi* (1985) 685.
12. I. HIGAHSI, Y. TAKAHASHI and T. ATODA, *J. Crystal Growth* **33** (1976) 207.

Received 5 September
and accepted 12 November 1986