Synthesis of Pure YB₄ Powder via the Reaction of Y₂O₃ with B₄C

Junguo Li,[†] Aiyi Peng, Yong He, Huiping Yuan, Qilong Guo, Qiang Shen, and Liangmeng Zhang

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

Pure YB₄ powder was synthesized via the reaction of Y_2O_3 with B₄C under a vacuum pressure within the range of 20–50 Pa using spark plasma sintering (SPS) route. The effect of temperature and the molar ratio of the starting materials was studied. The role of the YBO₃, an intermediate product, in the synthesis of YB₄ was investigated. For preparation of high purity YB₄, the molar proportion of B₄C to Y₂O₃ should not be higher than the stoichiometric ratio (15/7). YBO₃ can be removed through decomposing to Y₂O₃ and B₂O₃ or reacting with B₄C to form YB₄ and B₂O₃ at a temperature above 1650°C. The little residual impurities, such as Y₂O₃ and YBO₃, can be removed by hydrochloric acid washing. Thus, a high purity YB₄ powder has been synthesized. The oxygen content of the obtained YB₄ is about 0.007% and the particle size is in the range of 3–10 µm.

I. Introduction

Y TTRIUM tetraboride (YB₄) possesses some unique properties, such as high melting point(2800°C), high hardness and strength, excellent chemical stability, and good electrical and magnetic properties,¹⁻⁵ which makes it suitable for application in some extreme (ultra high temperature, nuclear, etc.) environments.

Yttrium tetraboride is not commercially available and the synthesis method of YB_4 has not been widely explored. Until now, only a few methods, such as solid-state reaction method between the elements, borothermic reduction method, and aluminothermal method have been reported.^{1,3–9} In the solidstate reaction method between the elements, the use of raw materials including the pure metal Y and B results in the high cost. The same disadvantage exists in the borothermic reduction method, whereas in the aluminothermal method, more impurities, such as the impurity of alumina, are introduced in the complex, high cost process. Recently, boron carbide/carbothermal reduction method was applied to synthesize YB₄ ceramics. Zaykoski⁵ prepared YB₄ ceramics by firing the mixture of Y₂O₃ and B₄C or B₄C/C at 1800°C for 2 h. However, some impurities, such as YBO3 and YB_2C_2 , are present in the ceramics, and the reaction process is still not clear. In this study, YB₄ was synthesized using Y₂O₃ and B₄C as starting materials, the effect of temperature and the proportion of starting materials on the reaction between Y_2O_3 and B_4C was investigated.

II. Experimental Procedure

The raw materials used in this study were as follows: Y_2O_3 powder (purity > 99.9%, 2–5 µm; Jiarun advanced materials

Co. Ltd, Ganzhou, Jiangxi, China) and B_4C powder (purity > 99.9%, 10 µm; Alfa Aesar Co. Ltd., Ward Hill, MA).

Firstly, Y_2O_3 and B_4C powder were mixed in an agate mortar in different molar ratios as shown in Table I. Then the mixtures were pressed into pellets and placed in a graphite die, and then sintered for 30 min at different temperatures using spark plasma sintering (SPS) under an initial vacuum pressure of 20 Pa. YBO₃ powder was synthesized by the reaction between Y_2O_3 and H_3BO_3 . The YBO₃ powder was added to YB₄ or B_4C and held for 30 min at different temperatures to research the role of YBO₃ in the synthesise processing of YB₄. The phase compositions of synthesized powder were analyzed using X-ray diffraction (XRD; Rigaku Ultima III, Tokyo, Japan). The morphology was observed using a scanning electron microscope (SEM; Hitachi 3400N, Tokyo, Japan). The oxygen content was detected using an oxygen analyzer (Model TC600; Leco, St. Joseph, MI).

III. Results and Discussion

Figure 1 shows the effect of temperature on the synthesis of YB₄. After treatment at 1500°C for 30 min, the starting materials, B₄C and Y₂O₃ can be found still in the sample, indicating that the reaction (Eq. (1)) cannot complete under this condition. In this sample, some yttrium borates, such as YBO₃, appear due to the reaction between the starting powder Y₂O₃ and the B₂O₃ produced from the reaction (1).^{10,11} A small amount of YBO₃ still remains in the sample fired at 1600°C and totally disappears after being treated at 1700°C. The results show that the temperature plays an important role in the transition of YBO₃ to YB₄.

$$7Y_2O_3 + 15B_4C = 14YB_4 + 15CO + 2B_2O_3.$$
 (1)

To reveal the change in YBO₃ during the heating, 20 vol% YBO₃ is mixed with B_4C or YB₄, and then the mixtures are treated at 1500°C-1700°C for 30 min. The XRD patterns of the products are shown in Figs. 2 and 3, respectively. After treated at 1500°C, the mixture of YBO3 and YB4 does not have any phase change (Fig. 2). The content of YBO3 decreases and the Y_2O_3 content increases with the rise in temperature above 1600°C. The results show that YBO₃ can decompose to Y_2O_3 and B_2O_3 above 1600°C (Eq. (2)). The vapor pressure of B_2O_3 as a function of temperature has been given by Eq. (3).¹² The nominal pressure maintained during the SPS process ranged 20–50 Pa. From Eq. (3), the vapor pressure of B_2O_3 reaches the pressure at 1340–1400°C. Therefore, B₂O₃ should boil at 1400°C and above, and then B_2O_3 can evaporate from the pellet and be removed using the pumped vacuum, with Y_2O_3 left in the sample. From Fig. 3, we can see that YBO₃ can react with B₄C to form YB₄ at 1500°C (Eq. (4)). However, the reaction is not completed after 30 min at 1500°C and 1600°C (there are still YBO₃ in the products). Above 1650°C, another reaction (Eq. (5)) can occur to form YB₆ whereas YBO₃ disappears. These results indicate that YBO₃ can be removed at a temperature above 1650°C. When the B₄C is insufficient, the excessive YBO₃ will transform to Y_2O_3 . When B_4C is

J. Zaykoski-contributing editor

Manuscript No. 30700. Received November 20, 2011; approved April 16, 2012. *Author to whom correspondence should be addressed. e-mail: lijg000@126.com





Fig. 1. X-ray diffraction patterns for the productions fabricated at different temperatures from the B_4C and Y_2O_3 mixture with a molar ratio in 2.1.



Fig. 2. X-ray diffraction patterns for mixture of 20 vol% YBO_3 and 80 vol% YB_4 heated to various temperatures.

excessive, YBO₃ will transform to YB₄ or YB₆. In both cases, the evaporation of B_2O_3 is necessary. The evaporation of B_2O_3 depends on the temperature, the vacuum pressure, and the time. Under the experimental vacuum pressure, B_2O_3 should boil. If the temperature has reached the temperature at which the reaction (2) (4) and (5) can occur, the B_2O_3 produced can be easily removed using the pumped vacuum, meanwhile YBO₃ is removed.

$$2YBO_3 = Y_2O_3 + B_2O_3$$
(2)

$$\log p_{\mathbf{B}_2\mathbf{O}_3}(atm) = 8.244 - \frac{19236}{T}$$
(3)¹²

$$14YBO_3 + 15B_4C = 14YB_4 + 15CO + 9B_2O_3$$
(4)

$$2YBO_3 + 3B_4C = 2YB_6 + 3CO + B_2O_3$$
(5)



Fig. 3. X-ray diffraction patterns for mixture of 20 vol% YBO_3 and 80 vol% B_4C heated to various temperatures.



Fig. 4. X-ray diffraction patterns of the productions obtained using sintering at 1700°C for 30 min from different molar ratio of B_4C to Y_2O_3 . S1:2.1, S2:2.2 and S3:2.3.

Figure 4 shows the XRD patterns of the products obtained using sintering at 1700°C for 30 min from different molar ratios of starting materials. The main phase is YB_4 in all the samples. However, in sample S1 and S2, Y₂O₃ phase is detected, indicating that Y2O3 cannot completely react with B_4C and transform to YB_4 . The oxygen content in the three samples is 1.78%, 0.61%, and 0.41%, respectively, decreasing with the increase in the molar ratio between B₄C and Y₂O₃. In sample S2 and S3, a few B₄C particles can be observed (Fig. 5), indicating that B_4C is excessive. According to the reaction between B_4C and Y_2O_3 (Eq. (1)), the stoichiometric ratio should be 15/7. In sample S2 and S3, the ratio of B_4C to Y_2O_3 is higher than this value and then the excessive B₄C remains in the products. For preparation of high purity YB₄, the ratio of B₄C to Y₂O₃ in the starting materials should be lower than the stoichiometric ratio, as B₄C cannot be easily removed using common mechanical or chemical methods whereas Y_2O_3 can be removed by washing with acid.

After grinding, the production of S1 was placed in hydrochloric acid (2 mol/L) and heated to 60°C with continuous stirring for 2 h. Then the powder was washed by distilled water for 3–5 times until it appears neutral. After being dried



Fig. 5. Backscatter electron images for sample S2 (a) and S3 (b). The arrow points to B_4C particles (dark area).



Fig. 6. XRD pattern (a) and SEM image (b) for the obtained YB₄.

in an oven at 100°C for 2 h, YB₄ powder was obtained. Fig. 6(a) shows the XRD patterns of the synthesized YB₄. There were only YB₄ peaks in the XRD pattern, showing that the Y₂O₃ was removed by hydrochloric acid washing. Y₂O₃ can react with HCl to transform into water-soluble YCl₃, which can be removed by water washing. Moreover, YBO3 also dissolves in hydrochloric acid and can be removed by water washing. Accordingly, even if there are a few residual YBO₃, it also can be removed. However, YB₄ shows chemical stability in hydrochloric acid. Consequently, YB_4 powder is obtained. The oxygen analysis shows that the oxygen content is only about 0.007%, indicating that the high purity YB₄ powder has been synthesized. The obtained YB₄ powder has brown color and is irregular in shape with a particle size in the range of 3-10 µm [Fig. 6(b)].

IV. Summary

Yttrium tetraboride can be synthesized from the raw materials Y₂O₃ and B₄C. For preparation of high purity YB₄, the molar proportion of B_4C to Y_2O_3 should not be higher than the stoichiometric ratio (15/7). The removal of the impurity YBO₃, an intermediate product, determines the yield and the purity. YBO3 can be removed through decomposing it to Y_2O_3 and B_2O_3 or react it with B_4C to form YB_4 and B_2O_3 at a temperature above 1650°C. When the vacuum pressure is lower than the vapor pressure of B_2O_3 , B_2O_3 can be removed quickly. A few residual impurities, such as Y₂O₃ and YBO3, can be removed by hydrochloric acid washing. A high purity YB₄ powder has been synthesized by treating the mixture of B₄C and Y₂O₃ with a molar ratio in 2.1 at 1700°C for 30 min under a vacuum pressure of 20-50 Pa and followed by a hydrochloric acid washing. The oxygen content

of the obtained YB_4 is ~0.007% and the particle size is in the range of 3-10 µm.

References

¹B. Jager, S. Paluch, W. Wolf, P. Herzig, O. J. Soga, N. Shitsevalova, and Y. Paderno, "Characterization of the Electronic Properties of YB4 and YB6 Using ¹¹B NMR and First-Principles Calculations," J. Alloys Compd, 383 $\begin{bmatrix} 1-2 \end{bmatrix} 232-8 (2004).$

A. Waśkowska, L. Gerward, J. Staun Olsen, K. Ramesh Babu, G. Vaitheeswaran, V. Kanchana, A. Svane, V. B. Filipov, G. Levchenko, and A. Lyaschenko, "Thermoelastic Properties of ScB₂, TiB₂, YB₄ and HoB₄: Experimental and Theoretical Studies," Acta Mater., 59 4886-94 (2011).

³G. A. Kudintseva, G. M. Kuznetsova, V. P. Bondarenko, N. F. Selivanova, and V. Ya. Shlyuko, "Preparation and Emissive Properties of Some Yttrium and Gadolinium Borides," *Powder Metall. Met. Ceram.*, **7** [2] 115–20 (1968).

⁴R. M. Manelis, G. A. Meerson, N. N. Zhuravlev, T. M. Telyukova, A. A. Stepanova, and N. V. Gramm, "Vacuum-Thermal Preparation of Yttrium and Gadolinium Borides, and Some of Their Properties," Powder Metall. Met. Ceram., 47 [11] 904-9 (1966).

⁵J. A. Zaykoski, M. M. Opeka, L. H. Smith, and I. G. Talmy, "Synthesis and Characterization of YB₄ Ceramics," *J. Am. Ceram. Soc.*, **94** [11] 3605–28 (2011). ⁶J. Bauer and H. Nowotny, "The Ternary System Yttrium-Boron-Carbon

(Der Dreistoff Yttrium-Bor-Kohlenstoff)," Chemical Monthly (Monatshefte fur Chemie), 102 1129–45(1971).

⁷N. N. Greenwood, R. B. Parish, and P. Thornton, "Metal Borides," *Q. Rev. Chem. Soc.*, **20** 441–64 (1966). ⁸A. Iltis and P. Maestro, "Preparation of Rare Earth Borides"; US Patent

No. 4999176, 1991.

⁹S. Otani, Y. Xuan, Y. Yajima, and T. Mori, "Flux Growth of YB₄ Crystals and Their Magnetic Properties," J. Alloys Compd., 361 1-3 (2003).

¹⁰J. Madarász, E. Beregi, J. Sztatisz, I. Földvári, and G. Pokol, "Combined DTA and XRD Study of Sintering Steps Towards YAl₃(BO₃)₄," *J. Therm.*

Anal. Calorim, **64** [3] 1059–65 (2001). ¹¹M. Sweeney, "Thermochemical Studies of Group IIIB Borates and Mixed Borates," Thermochim. Acta, 11 [4] 397–407 (1975).

²S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Pressureless Densification of Zirconium Diboride With Boron Carbide Additions," J. Am. Ceram. Soc., 89 [5] 1544-50 (2006).